Chemistry and Technology of Explosives

VOLUME 4

Chemistry and Technology of Explosives

Volume 4

by

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PERGAMON PRESS
Member of Maxwell Macmillan Pergamon Publishing Corporation

OXFORD · NEW YORK · BEIJING · FRANKFURT
SÃO PAULO · SYDNEY · TOKYO · TORONTO

U.K.
Pergamon Press plc, Headington Hill Hall,
Oxford OX3 0BW, England

U.S.A.
Pergamon Press Inc., Maxwell House, Fairview Park,
Elmsford, New York 10523, U.S.A.

PEOPLE'S REPUBLIC OF CHINA
Pergamon Press, Room 4037, Qianmen Hotel, Beijing,
People's Republic of China

FEDERAL REPUBLIC OF GERMANY
Pergamon Press GmbH, Hammerweg 6,
D-6242 Kronberg, Federal Republic of Germany

BRAZIL
Pergamon Editora Ltda, Rua Eça de Queiros, 346,
CEP 04011, Paraiso, São Paulo, Brazil

AUSTRALIA
Pergamon Press Australia Pty Ltd., P.O. Box 544,
Potts Point, N.S.W. 2011, Australia

JAPAN
Pergamon Press, 5th Floor, Matsuoka Central Building,
1-7-1 Nishishinjuku, Shinjuku-ku, Tokyo 160, Japan

CANADA
Pergamon Press Canada Ltd., Suite No. 271,
253 College Street, Toronto, Ontario, Canada M5T 1R5

First English edition 1964
Reprinted (with corrections) 1983
Reprinted 1988 , 1990

Library of Congress Cataloging in Publication Data

(Revised for vol. 4)
Urbański, Tadeusz.
Chemistry and technology of explosives.
Translation of: Chemia i technologia materiałów wybuchowych.
Vol. 3 translated by Marian Jurecki, edited by Sylvia Laverton.
Includes bibliographies and indexes.
1. Explosives. I. Laverton, Sylvia. II. Title
TP270.U713 1965 662'.2 83-2261

British Library Cataloguing in Publication Data

Urbański, T.
Chemistry and technology of explosives.
Vol. 4
1. Explosives
I. Title
662'.2 TP270
ISBN 0-08-026206-6

Printed in Great Britain by
Antony Rowe Ltd, Chippenham, Wiltshire

PREFACE

Since 1964–67 when the previous three volumes of *Chemistry and Technology of Explosives* appeared, considerable progress has been made in the field of the science of explosives – the science in a broader sense which includes not only the theoretical knowledge of explosives but also their manufacture, problems of safety in the manufacturing processes and handling.

As in the previous three volumes the author limited his text to *chemistry* and *technology* of explosives. The problems of the theory of detonation and analytical ones are not discussed here and are only touched as much as it was needed to understand the properties of explosives. Thus in the 'Introduction' chapter a description is given of the relationship between the chemical structure and the parameters of the explosive properties, as this refers to the structural problems of organic substances possessing such properties.

However, the author wishes to point out that he is not giving the full review of the existing progress for some particular reasons – a general philosophy for Peace in the World and some personal reason as a former POW. He is completely against the use of explosives for military purposes and has dedicated his book to peaceful applications.

The author wishes to quote from the book by S. Fordham, *High Explosives and Propellants* (Pergamon Press): "The explosives technologist, who has usually seen and perhaps even experienced the effects of explosives is the last to want war or for his products to be used for warlike purposes. It is no accident that Nobel who founded the modern explosives industry also founded the Peace Prize associated with his name".

Once more the author would like to repeat what he said in the preface to his book in 1964–67: "... more explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives." Nevertheless, following this line of thought no mention is made in this book on shells, projectiles, fuses etc., or other parts of military weapons. However it is still difficult to distinguish between military and peaceful application of military weapons. Here are a few examples:

> Gas burning from a newly drilled oil pit in Karlin in Northern Poland in 1981 was successfully extinguished with howitzer shells; the danger of an avalanche of snow can be prevented by firing special guns with shells filled

with high explosives; firing rockets with explosives loaded with silver iodide is in use for promoting rain (Vol. III, p. 324). Silver iodide dispersed in higher layers of atmosphere by anti-aircraft rounds is in use in the U.S.S.R., according to "*TWA Ambassador*" (p. 37, May 1981).

A conscientious attempt has been made to cover the available literature on the subject, however not every paper and report has been mentioned as it was considered to be of greater value to couple a reasonably comprehensive coverage with a critical assessment of the available information and not to describe every paper. The excellent *Encyclopedia of Explosives* and related items produced by (the late) B. T. Fedoroff, O. E. Sheffield and S. M. Kaye should be consulted for the whole literature on explosives.

Also excellent reviews have appeared in Volumes of *Annual Reviews of Applied Chemistry*, Issued by Society of Chemical Industry, London, between 1950 and 1975, written by J. Taylor, E. Whitworth, W. E. Batty, I. Dunstan and a number of authors from I.C.I. Ltd.

The author apologises to the authors for any important work overlooked in the present volume.

It is the pleasant duty of the author to thank all the colleagues who responded to his request for information. I am most grateful to them. They were from:

(1) Federal Republic of Germany: Dr A. Homburg (Köln), Dr R. Meyer (Essen), Dipl. Ing. H. Plinke (Bad Homburg), Dr H. Schubert and Dr Fred Volk (Pfingstal).
(2) France: Ingénieur A. Delpuech (Sevran), Ingénieur Général P. Tavernier (Paris).
(3) Holland: Professor Th. J. de Boer (Amsterdam).
(4) India: Dr A. K. Chatterjee (Hyderabad) and Dr S. P. Panda (Poona).
(5) Japan: Mr K. Yamamoto (Asa), Professor T. Yoshida (Tokyo).
(6) Italy: Dr E. Camera (Udine).
(7) Sweden: Dr Jan Hansson (Sundbyberg), Dr G. A. Wetterholm (Göteborg).
(8) Switzerland: Mr Guido Biazzi, Dr G. S. Biasutti and Dr A. Fauci (Vevey).
(9) U.K.: Mr A. Brewin, M.A. (ERDE, Waltham Abbey).
(10) U.S.A.: Professor J. F. Bunnett (Santa Cruz, Cal.), Mr C. L. Coon (Livermore, Cal.), Professor J. A. Concling (Chestertown, Md.), Professor H. Feuer (Lafayette, Ind.), Dr Mortimer J. Kamlet (Silver Spring, Md.), Professor Nathan Kornblum (Lafayette, Ind.), Dr A. T. Nielsen (China Lake, Cal.), Professor G. A. Olah (Los Angeles, Cal.), Professor Glen A. Russell (Ames, Iowa), Dr R. W. Van Dolah (Pittsburgh, Pa), S.M. Kaye (Dover, New Jersey).
(11) U.S.S.R. (Moscow): particularly to the late Professors K. K. Andreev and S. S. Novikov, Professors V. I. Pepekin and V. V. Sevostyanova and

Dr G. T. Afanasyev, Dr G. N. Bezpalov, Professor V. K. Bobolev, Professors L. V. Dubnov and A. P. Glazkova, Dr B. N. Kondrikov, Professor V. V. Perekalin (Leningrad).

(12) Poland: the late Professor W. Cybulski/Mikołów/, Dr T. Krasiejko, Dr R. Kuboszek, Dr K. Lewańska, Dr T. Mrzewiński, Dr M. Parulska, Dr W. Sas, Professor M. Witanowski and Mr M. Ziółko – all from Warsaw, and the Directors of the Institute of Organic Industry, Warsaw: Prof. S. Fulde, Dr W. Moszczyński and Mrs J. Zołedziowska for their assistance.

My thanks are due to Dr R. Kuboszek for his help in the proof reading and preparing the subjects index.

The author thanks industrial firms which supplied him with most valuable information on their processes and apparatus. They are: Dr Ing. Mario Biazzi S.A., CH-1800 Vevey, Switzerland; Bofors Nobel Chematur, S-69020 Bofors, Sweden; Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Wahldorf, Dynamit Nobel A.G., D-5000 Köln, Jenaer Glasswerk, Schott u.Gen., D-6500 Mainz, in FRG; Kemira OY, Vihtavuori, Finland; Maschinenfabrik Fr. Niepmann G.m.b.H., D-5520 Gevelsberg, Westfalen FRG; Nitro-Nobel A.B., S-7103 Gyttorp, Sweden; Adolf Plinke Söhne, D-638 Bad Homburg, Wasag Chemie Sythen G.m.b.H. D-4358 Haltern, Westfalen, and Werner & Pfleiderer, D-7000 Stuttgart, FRG; Nippon Kayaku Co. Ltd, Asa, Japan; S.A.PRB-Nobel-Explosifs, B-1960, Sterrebeck, Belgium; U.S. Bureau of Mines (Washington D.C.); IDL Chemicals Ltd, Hyderabad, India.

The author is also grateful for the permissions received to reproduce the pictures, diagrams and text from books and journals published by:

1. American Chemical Society,
2. Department of Defence, Dover, N.J., U.S.A.,
3. John Wiley and Sons, Inc., New York,
4. Plenum Press, New York,
5. Verlag Chemie, Weinheim, FRG.

Finally my thanks are due to Mr I. Robert Maxwell, M.C., Chairman of Pergamon Press Ltd, Oxford, Mr Alan J. Steel, Publishing Director, Dr Colin J. Drayton, Senior Managing Editor and Mr Peter A. Henn, Senior Publishing Manager of Pergamon Press, and Mrs Eileen Morrell for tidying up my 'foreign' English.

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INTRODUCTION

(Vol. I, p. 1)

NOVEL INFORMATION ON EXPLOSIVE PROPERTIES

It has been shown that some non-explosive organic and inorganic substances can explode when subjected to the action of very high pressure. This was recorded for the first time by Bridgman [1]. Teller [2] tried to find an explanation in terms of the activation energy which should be lowered with increased pressure.

More recently Malmrud and Claesson [3] examined the behaviour of a number of compounds at a pressure of 35,000 kg/cm^2. They found that some acids, such as oxalic acid hydrate malonic, tartaric and citric acid, and other common substances such as aspirin, sucrose, polystyrene and calcium chloride, exploded when high pressure was released. A number of substances (e.g. succinic, glutaric, adipic, maleic, fumaric, phthalic acids) did not show this behaviour. According to the authors they did not explode because they required higher pressure.

The explanation given by Malmrud and Claesson is similar to that given by Bridgman. They believe that over a critical pressure, which depends on the coefficient of friction, plastic flow stress and disc thickness, the sample becomes mechanically unstable when pressure is released and is violently expelled.

Polystyrene was simultaneously carbonized which was probably caused by an increased temperature due to heating by friction.

The author of the present book is inclined to rationalize that under very high pressure considerable deformation of the crystal-net can occur and the atoms are approaching distances which produce their repulsion.

The problem arises as to whether explosives can be brought to explosion by high static pressure. So far the only published paper [4] indicated that nitromethane, perdeuteronitromethane and a few dinitroalkanes cannot explode at static pressure up to 50 kbar.

It is known that acetylenic bond possesses endothermic characteristics (Vol. III, p. 227) and it is interesting to point out that a number of acetylenic compounds were found in nature as early as 1889 [5] and 1892 [6]. Currently important are the works of E. R. H. Jones [7] and Bohlmann [8] who isolated and established the structure of numerous naturally occurring polyacetylenes and confirmed their structure by synthesis. Most of the polyacetylenes possess explosive properties.

Some hydroxylamine derivatives also show explosive properties. The simplest of them is fulminic acid which can be regarded as an oxime of carbon monoxide (Vol. III, p. 133). Lossen [9] has found that oxalohydroxamic acid $(CONHOH)_2$ possesses explosive properties. Nitrogen sulphide N_4S_4 – a formal analogue of NO – possesses explosive properties. It explodes on heating to its m.p. 178°C or on shock [78].

A surprising discovery was made in 1963 by several authors almost simultaneously and independently. This was that xenon trioxide possesses well marked explosive properties. Thus N. Bartlett and Rao [10] while dissolving xenon tetrafluoride in water, observed a vigorous reaction with the evolution of hydrogen fluoride. Evaporation of the solution *in vacuo* at room temperature left a white solid which exploded vigorously when warmed *in vacuo* above 30° or 40°C.

D. F. Smith [11], Williamson and Koch [12] obtained the same compound by hydrolysing xenon hexafluoride and mentioned its explosive properties and described it as xenon trioxide. Templeton and co-workers [13] definitely established by X-ray analysis that the white crystalline, non-volatile explosive was xenon trioxide. It can best be prepared by hydrolysing xenon hexafluoride:

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF. \qquad (1)$$

The explosive properties of the substance can be explained by the strongly endothermic character of the substance [14]:

$$-\Delta H_f = -90 \text{ kcal/mol.}$$

The search for novel ingredients of rocket fuels led to the discovery of new groups producing explosive properties. One of them was the perchloryl group (ClO_3), the compounds containing it are described in Vol. II, p. 488.

A new class of explosives which might possess some practical importance are compounds of the difluoroamino group: NF_2. Their first representatives were obtained by Lawton and co-workers [15] and Grakauskas [16]. A special chapter (p. 270) is dedicated to this group of compounds.

CALCULATION OF DETONATION PROPERTIES OF EXPLOSIVES

It is well known that the calculation of some constants, characterizing properties of explosives, starts from their decomposition equations. Such are: enthalpy of decomposition and of formation, volume of gaseous products, their temperature and so called specific pressure *f*. These constants are used extensively to estimate the properties of high explosives (*HE*) and propellants. Other very important constants of *HE* are: the velocity of detonation under given experimental conditions or maximum velocity of detonation. D_{max}, and pressure in the front of the detonation wave.

With the advent of the development of the hydrodynamic theory of detonation, based on the concepts of Chapman [17] and Jouguet [18], it was possible to calculate the velocity of detonation. The pioneering work was done by A. Schmidt [19] and his method was improved by a number of authors. Critical reviews of the methods have been described in a number of monographs: Cook [20], Zeldovich and Kompaneets [21], Andreev and Belyaev [22], Johansson and Persson [23], Fickett and Davis [24].

The problems connected with the hydrodynamic theory of detonation are outside the scope of this book and only papers dealing with the correlation between the structure of explosives and their power will be given here. Originally the papers were directed to correlate the oxygen balance (OB) with the 'explosive power'. This was initiated by Lothrop and Hendrick (Vol. I, p. 2) and met with a well founded criticism (A. Schmidt, Vol. I, p. 2). The criticism was based on the fact that oxygen in nitro groups has a different thermochemical function than that of carboxylic and hydroxylic groups. The discussion aroused much interest in the attempt to introduce a differentiation of oxygen atoms.

The first of the kind were papers by Martin and Yallop [25a, b]. They proposed a 'corrected OB' calculated as follows:

$$\mathrm{OB} = \Omega = (z - 2x - y/2)\,100/n \pm 100\,w/n, \qquad (2)$$

where: x, y, z are the respective numbers of atoms of carbon, hydrogen and oxygen in the molecule,

n – the number of atoms in the molecule,
w – summation of O atoms according to their linkages, thus:
w = O for oxygen atoms in NO_2 groups in *C*-nitro, *O*-nitro and *N*-nitro compounds,
w = 1 for oxygen C—O—N in *O*-nitro compounds,
w = 1.8 for oxygen C=O in carboxylic groups,
w = 2.2 for oxygen in phenols and alcohols. ± Is taken: + if the first term is +, and − if the first term is −.

The rate of detonation D was calculated from semiempirical equation (3) [25a].

$$D_{\mathrm{calc}} = 2509 + 13.25\,\Omega + 3793\,\rho + 12.81\,\rho\,\Omega \qquad (3)$$

where: ρ is the density of the explosive (g/cm^3).

In another equation they introduced the value H cal/g of the heat of formation [25b].

The work of Martin and Yallop was met with criticism. Thus Price [26] concluded that OB cannot determine the heat of explosion or detonation and the rate of detonation cannot be a linear function of OB. Roth [27] pointed out that the correlation between Martin and Yallop's 'corrected OB' is successful only for a restricted group of similar explosives. The correlation breaks down for explosives with a positive OB. He concluded that "OB is a concept that can provide useful qualitative information. It should not be used for quantitative correlation except . . . for chemically similar explosives."

A number of authors: Głowiak [28], Mustafa and Zahran [29] and Pagowski [30] tried to extend the method of Martin and Yallop. In particular Pagowski's work merits attention. He attempted to correct equation (2) of Martin and Yallop suggesting the 'effective oxygen balance' B:

$$B = (z - 2x - \frac{y}{2} \pm P)\, 100/n. \tag{4}$$

P is the correction accounting for energy gains or losses from the actual chemical structure of the compound while taking into account different oxygen atoms: those which are already bonded with carbon ($C{=}O$, $C{-}O{-}N$) and those (NO_2) which are free to develop the exothermic reaction of oxidation.

For the rate of detonation Pagowski gave a semi-empirical equation (5):

$$D = 8600 \pm 32.7\, B \tag{5}$$

at $\rho = 1.6$.

According to Pagowski the calculated values of D fit well to experiments – Table 1.

TABLE 1. Experimental and calculated values of D

Explosive	D_{exp}	D_{calc}
TNT	6980	6345
Tetryl	7450	7505
EDNA (III, 18)	7920	7900
Cyclonite (RDX)	8200	8185
PETN	7820	7880

Later a remarkable semi-empirical method of calculating the detonation pressure and velocity was given by Kamlet and co-workers [31].

Kamlet and Jacobs [31a] have shown that the detonation pressure and velocity of $C{-}H{-}N{-}O$ explosives can be calculated at their initial densities above 1 g/cm^3 while using the following simple empirical equations:

$$P = 15.58\, \varphi\, \rho^2 \tag{6}$$

$$D = 1.029\, \varphi\, (1 + 1.30\, \rho_0)^2 \tag{7}$$

$$\varphi = NM^{1/2}\, Q^{1/2}, \tag{8}$$

where:

P is the pressure in kbar,
D the detonation velocity in m/s,
N the number of moles of gaseous detonation products per gram of the explosive,
M the average weight of these gases in g/mol,
Q the chemical energy of the detonation reaction (enthalpy $-\Delta H_0/pg$),
ρ = the initial density.

A few examples of the calculation of the velocity of detonation [25d] which give an average error of *ca.* 1% only, are given in Table 2.

TABLE 2. Experimental and calculated rates of detonation

Explosive		D_{exp}	D_{calc}	% deviation ($D_{calc}-D_{exp}$)
TNT	1.64	6950	6959	+0.1
	1.445	6484	6395	−1.4
	1.30	6040	5977	−1.0
	1.00	5100	5111	+0.2
Picric acid	1.71	7350	7360	+0.1
	1.25	6070	6000	−1.2
Ammonium picrate	1.55	6850	6798	−0.8
Tetryl	1.70	7560	7681	+1.6
EDNA (III, 18)	1.562	7750	7789	+0.5
RDX (Cyclonite)	1.80	8754	8780	+0.3
	1.60	8060	8098	+0.5
	1.20	6750	6731	−0.3
HMX	1.90	9100	9117	+0.2
	1.84	9124	8913	−2.3
	1.77	8500	8671	+2.0
PETN	1.77	8600	8695	+1.1

A few examples of the calculation of Chapman-Jouguet pressure are given below – Table 3 [31c]. The Kamlet method is very useful for the rapid calculation of most important constants characterizing high explosives.

Other remarkable methods of calculating parameters of detonation have been developed by Pepekin, Lebedev and associates [32, 33]. They worked out [32] a method of calculation of heat of detonation when two factors are known: the bulk formula of the explosive and the enthalpy of formation ΔH_f^0. The following are semi-empirical equations for an explosive $C_aH_bO_cN$:

$$Q_{max} = \frac{28.9\,b + 470\,(c - b/2) + \Delta H_f^0}{MW} \qquad (9)$$

TABLE 3. Calculation of pressure developed by detonation

Explosive		P_{exp} kbar	P_{calc}	% deviation ($P_{calc}-P_{exp}$)
TNT	1.62	212	197.8	−6.7
	1.30	123	127.4	+3.6
	1.14	94	97.9	+4.1
RDX	1.80	347	342.5	−1.3
	1.63	283.7	280.8	−1.0
	1.40	213	207.1	−2.8
	1.20	152	152.2	+0.1
HMX	1.90	393	380.9	−3.1
PETN	1.77	350	332.1	−5.1
	1.67	300	295.7	−1.4
Tetryl	1.70	263	252.8	−3.9

where:

Q_{max} is the maximum possible heat of detonation in kcal/kg,
MW is the molecular weight of the compound.

The heat of detonation at the density ρ g/cm^3 is Q_ρ, and equation (10) makes it possible to calculate:

$$Q_\rho = Q_{max}\ [1-(0.528-0.165\rho)(1.4-\alpha)] \tag{10}$$

where: α is 'oxygen coefficient' calculated from equation (11):

$$\alpha = \frac{c}{2a+2b/2} \tag{11}$$

When

$$\alpha \geqslant 1.4,\ Q_\rho = Q_{max}.$$

Another more complicated formula was worked out for explosives with a high content of hydrogen and low value of α, for example $\alpha < 0.4$.

The calculated figure for some common explosives are given in Table 4.

The average deviation is 2.3% and at $\rho > 1.0$ it is 1.8%.

In another paper Pepekin, Kuznetsov and Lebedev [33] worked out more complicated equations which made it possible to calculate the rate of detonation of explosives with a bulk formula $C_a\ H_b\ O_c\ N_d\ F_e$ at a given density ρ_1 g/cm^3.

The following are equations given by these authors:

$$K_{BB}\ \frac{0.135\,a\,\frac{a}{a+b} + 21\,b\,\frac{b}{a+b} + 0.4\,(c+d+e)}{MW} \tag{12}$$

TABLE 4. Calculated and experimental data for the heat of detonation

Compound		Q_{calc}	Q_{exp} kcal/kg	Q_{max}
TNT	1.00	830	860	1288
	1.60	1000	1030	
Picric acid	0.90	880	830	1282
	1.70	1030	1010	
Tetryl	0.98	980	960	1431
	1.69	1150	1160	
Nitroguanidine	0.80	970	980	1102
	1.58	1030	1060	
Cyclonite (RDX)	1.10	1160	1190	1481
	1.70	1280	1290	
Octogene	1.30	1200	1210	1477
	1.80	1300	1300	
PETN	0.90	1260	1300	1526
	1.70	1340	1350	

and

$$n = K_{BB}\, \rho_1^{1/2} \tag{13}$$

where:

K_{BB} – the coefficient of the composition of the compound,
n – the number of molecules in the products of the detonation,
ρ_1 – the density of the explosive.

The rate of detonation D m/s can be calculated from formula (14)

$$D^2 = 8.0\,(Q + R) \tag{14}$$

where Q is the heat of detonation in kcal/kg calculated from formula (10),

$$R = \left(\frac{n}{n_z}\right)^3 \rho_1{}^2 \tag{15}$$

where n_z is the number of molecules in the products of detonation.

Pressure is calculated from equation (16):

$$P = \rho_1\, D^2\, (x_1 - 1)/x_1 \tag{16}$$

where x_1 is the experimental degree of compression in the front of the detonation wave where density is ρ:

$$x_1 = \frac{\rho}{\rho_1}$$

The calculated and experimental data for D and P are collected in Table 5. Mean deviation is *ca.* 1.4%.

TABLE 5. Calculated and experimental data for D and P

Compound	ρ_1	Q	κ_{BB}	x_1	D_{calc}	D_{exp}	P_{calc}	P_{exp}
					m/s		kbar	
TNT	1.64	1010	0.0202	1.38	6900	6940	215	220
Picric acid	1.80	1173	0.0207	1.37	7600	7700	297	
Tetryl	1.70	1150	0.0215	1.37	7480	7560	257	263
Nitroguanidine	1.70	820	0.0298	1.31	8140	8200	266	
Cyclonite (RDX)	1.802	1300	0.0260	1.34	8740	8800	349	347
Octogene (HMX)	1.903	1320	0.0260	1.33	9100	9150	390	393
PETN	1.77	1375	0.0243	1.36	8500	8370	338	350
TACOT	1.85	1044	0.0201	1.37	7310	7250	267	263

Recently Bernard [34] worked out a different formula for the rate of detonation based on his kinetic theory of detonation [35]. His equation for the correlation of the rate of detonation and the density ρ_1 in the shock wave front is as follows:

$$D_{max} = \frac{\rho_1}{\rho_{max}} \frac{k T_0}{h} d. \qquad (17)$$

D_{max} is the experimental rate of detonation at an infinite diameter and maximum density ρ_{max},
k the Boltzman constant,
h the Planck constant,
T_0 the initial temperature of the explosive,
d the mean molecular diameter.

Bernard applied his equation to a number of nitrate esters at room temperature.

Some of his results are shown in Table 6.

TABLE 6. Density in front of the shock wave and experimental rate of detonation

Substance	D_{max} m/s	ρ_{max}	ρ_1
Nitroglycerine	7700	1.6	2.57
Ethylene glycol dinitrate	8000	1.49	2.78
PETN	8600	1.77	2.94
Hexanitrate of dipentaerythrit	7450	1.63	1.93
Mannitol hexanitrate	8260	1.73	2.43
Methyl nitrate	8000	1.20	2.61

A plot of log D_{max} against log ρ_1 gives a straight line.

Bernard and co-workers [51] extended his calculations to the rate of detonation of *C*-nitro, *O*-nitro and *N*-nitro compounds by using two equations:

$$D_{\infty}^{\rho_{\max}} = \frac{\rho_1}{\rho_{\max}} \frac{k\,T_0}{h} \left(\frac{6M}{\pi N \rho_{\max}} \right)^{1/3} \tag{17a}$$

and

$$D^a = C_0\,(M/n) \tag{17b}$$

where:

h is the Planck constant,
M denotes the mean molecular mass of the products,
N Avogadro number,
C_0 concentration of molecules on the surface of the explosive,
n number of the nitro groups in the molecule,
a exponent varying from 1.5 to 2.

A characteristic feature of the calculation by Bernard is that he does not use the enthalpy of detonation but considers that the density ρ_1 in the shock front, that is, the compression by the shock wave is decisive for the rate of detonation. The groups 'explosofores', such as NO_2, N_3 are particularly strongly compressed. Thus $\rho_1/\rho_{\max}$ for dinitrobenzene is 1.40 and for picric acid is 1.88. For azides it is approaching 1.7.

Two more papers should be mentioned: that by Aizenshtadt [52] and one recently given by Rothstein and Petersen [53]. The latter authors like Bernard [34, 51] point out that a simple empirical linear relationship exists between the detonation velocity at theoretical maximum density and a factor F which solely depends upon chemical composition and structure.

Thus:

$$D' = D_0 + (\rho_{TM} - \rho_0) \times 3.0, \tag{18}$$

where

D' is calculated rate of detonation,
D_0 experimental rate of detonation,
ρ_{TM} theoretical maximum density,
ρ_0 experimental density.

Factor F can be calculated:

$$F = 100 \times \left[\frac{n(\mathrm{O}) + n(\mathrm{N}) - \frac{n(\mathrm{H})}{2n(\mathrm{O})} + \frac{A}{3} - \frac{n(B)}{1.75} - \frac{n(D)}{4} - \frac{n(E)}{5}}{\mathrm{MW}} \right] - G \tag{19}$$

where $G = 0.4$ for liquid and $G = 0$ for solid explosives. $A = 1$ if the compound is aromatic, otherwise $A = 0$ and MW = molecular weight.

The other expressions:

$n(\mathrm{O})$ = number of oxygen atoms,
$n(\mathrm{N})$ = number of nitrogen atoms,
$n(\mathrm{H})$ = number of hydrogen atoms,
$n(B)$ = number of oxygen atoms in excess of those already available to form CO_2 and H_2O,
$n(C)$ = number of oxygen atoms double bonded to carbon as in $C=O$,
$n(D)$ = number of oxygen atoms singly bonded directly to carbon in $C-O-R$ linkage where R = H, NH_4 or C.
$n(E)$ = number of nitrate groups either as nitrate-esters or nitrate salts.

The relation between D' and F can be expressed by the linear equation

$$D' = \frac{F-0.26}{0.55}. \tag{20}$$

The deviations between the calculated and experimental values in 95% of explosives is of the order of 5%. Some of the results are given in Table 7.

TABLE 7. Calculated and experimental data of D. Calculated values of the factor F

Substance	TM	D (calc)	F	D_0 (exp)	Deviation %
TNT	1.65	6960	3.93	6670	−4
TNB	1.64	7270	4.26	7270	0
Picric acid	1.76	7500	4.31	7360	−2
HNB	2.0	9500	5.27	9110	−4
Tetryl	1.73	7910	4.54	7780	−2
Nitroguanidine	1.72	8160	4.81	8270	+1
EDNA	1.71	8230	4.83	8310	+1
Cyclonite (RDX)	1.83	8850	5.18	8950	+1
Octogene (HMX)	1.90	9140	5.24	9050	−1
Nitroglycerine	1.60	7700	4.35	7440	−3
DGDN	1.38	6760	3.97	6750	0
PETN	1.77	8290	4.71	8090	−2
DINA	1.67	8000	4.63	7950	−1
TACOT	1.85	7250	4.14	7050	−3

It appears that the calculation of important parameters of detonation is still in progress and further improvements with two basic methods:

(1) taking into account the enthalpy of detonation,
(2) taking into consideration the kinetic theory of detonation.

The problems are tackled in a few monographs: the earlier ones: [54–60] and more recent by Fickett and Davis [24] and Mader [61].

Yoshida and co-workers [88] applied molecular orbital theory (Dewar's MINDO method) to calculate the heat of formation of explosives.

A more detailed discussion of the problems of the theory of high explosives are outside the scope of the present book.

SENSITIVITY OF EXPLOSIVES TO IMPACT

The experimental finding of Wöhler and Wenzelberg (Vol. I, p. 3) gives a general estimation of the sensitivity of nitroaromatic explosives to impact as a function of the character and number of substituents to the benzene ring. On the other hand T. Urbański [36] expressed the view in 1933 that the sensitivity of solid explosives to impact is a complicated function of a few factors, among which the most important are:

(a) sensitivity to high temperature,
(b) sensitivity to friction.

This was based on two observed factors:

(1) similarity of the curves of the sensitivity of mixtures of explosives to impact and sensitivity to temperature,
(2) the shape of the curves of sensitivity of solid mixtures to impact indicates that the sensitivity of mixtures is greater than that of the components due to the friction of particles of two different solid substances. In turn, the friction can obviously generate a high temperature (Bowden and Tabor [37]).

The related curves are given in Vol. III, pp. 250, 251, 262 and reproduced now in Fig. 1. Both curves (*T*-sensitivity to elevated temperature, *M*-sensitivity to impact) are clearly composed of two parts: I and II. (Curve *T* was established by determining the temperature of ignition of the samples of 5 g in test tubes placed in wood alloy at 150°C by increasing the temperature of the alloy at the rate of 10°C/min. The sensitivity to impact is expressed in ordinates as the work in kg/cm^2 produces 50% of explosion). The sensitivity to impact is manifest by a shape where fraction I of the curve *M* indicates the increase of the sensitivity of compound *A* by adding a less sensitive compound *B*. This is rationalized in terms of the friction between two foreign solid particles.

The sensitivity of mixtures to impact through friction is particularly noticeable in examples of mixtures of TNT with hard crystals of ammonium nitrate (Fig. 70, Vol. III, p. 262).

Papers have been published on the increase of sensitivity to impact by adding gritty compound, Ubbelohde *et al.* [38] and recently Scullion and McCormack [39].

Bowden and Yoffe [40] have developed the well known concept of 'hot spots' and that the initiation of explosion stems from 'hot spots' created by thermal factors and crystal hardness and shape. Small bubbles of air included in

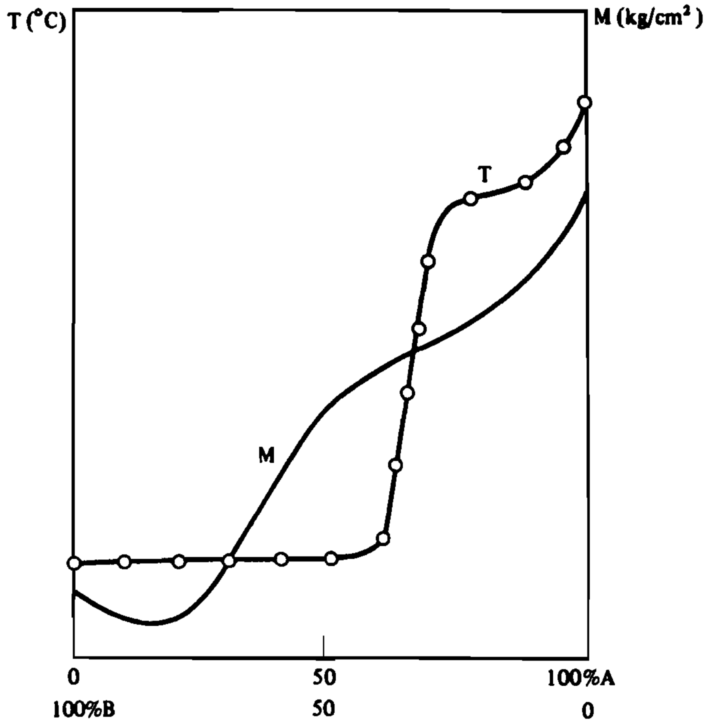

FIG. 1. Sensitivity to impact (*M*) and initiation temperatures (*T*) of mixtures of two explosive components: *A* and *B*. (According to T. Urbański [36]).

liquid explosives (e.g. nitroglycerine) also increase the sensitivity to impact through the adiabatic compression of air and a rapid increase in temperature. See also Lovecy [41].

Kamlet [42, 43] also agrees with the thermal character of the sensitivity to impact. He developed an ingenious method of calculating the sensitivity of explosives to impact. For similar explosives he found a linear relationship between logarithmic 50% impact heights and values of oxygen balance OB_{100}. The latter value is calculated for C—H—N—O explosives from the equation:

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{MW} \qquad (21)$$

where n_O, n_H, n_C represent the number of atoms of the respective elements in the molecule and n_{COO} is the number of carboxylic groups.

Fifty per cent impact heights on a logarithmic scale give a straight line.

A few figures are given (Table 8) for typical nitroaromatic compounds [42] and nitramines [43].

TABLE 8. Sensitivity of explosives to impact

Explosive	OB_{100}	h 50% (cm)
TNT	−3.08	160
TNB	−1.46	100
Picric acid	−0.44	87
Styphnic acid	+0.41	43
RDX (Cyclonite)	0	24
HMX	0	26
EDNA	−1.33	34

Cherville and associates [44] have examined a number of explosives in a mass spectrograph. Particularly important and reproducible were results at 77K. The formation of NO_2 was readily established in the spectrograms. The authors introduced a concept of the radiochemical yield G_{NO_2} of the formation of NO_2. A considerable difference exists between the values of G_{NO_2} of nitramines and nitroaromatics. They correlated the values of G_{NO_2} with those of the sensitivity of explosives to impact, friction and high temperature (temperature of initiation t_i at the rate of heating 5°C/min): Table 9.

TABLE 9. Sensitivity of explosives to impact and friction

Explosive	Sensitivity to impact kgm	Sensitivity to friction kgf	Difference between t_i and temp. of melting point t_m $t_i - t_m$	G_{NO_2}
PETN	0.31	4.5	79	3.8
RDX	0.45	11.5	56	0.9
Octogen (HMX)	0.52	10	50	0.8
Tetryl	1.1	27% at 36 kgf	111	0.006
Picric	3	7% at 36 kgf	178	0.001
TNT	48% at 5 kgm	29.5	209	0.001
Nitroguanidine	no explosion	no explosion	no inflammation	0

A very important contribution to the knowledge of the sensitivity of explosives to impact has been given by Delpuech and Cherville [45]. They came to the conclusion that the basic criterion of sensitivity of explosives lies in the distribution of electrons in their ground state and the comparison with that in the excited state. With the advent of quantum mechanical methods, and particularly that of I.N.D.O. [46] they were able to calculate the distribution of electrons in explosives, thus introducing a new and original criterion of sensitivity of explosives. For quantitative estimation they introduced a parameter $\Delta C^\circ/l$, where

ΔC^o is the dissymmetry of the distribution of electrons in the ground state,
l the length of the bond $C-NO_2$, $N-NO_2$ or $O-NO_2$.

The following are a few figures thus calculated (Table 10). Higher sensitivity of explosives is manifested by a higher $\Delta C^o/l$. The data for excited state $\Delta C^x/l$ were calculated with the method C.N.D.O-S/C.I. [47].

TABLE 10. Sensitivity of explosives to impact

Explosive	Bond*	C^o	$\frac{C^o}{l}$	$\frac{C^x}{l}$
DNB	$C(1)-NO_2$	0.539	0.363	0.308
TNB	$C(5)-NO_2$	0.575	0.391	0.303
RDX	$N(1)-NO_2$	1.044	0.764	0.343
HMX (δ)	$N(1)-NO_2$	0.937	0.673	0.345
EDNA	$N-NO_2$	0.880	0.676	0.499
Tetryl	$N-NO_2$	0.841	0.624	0.478
PETN	$O-NO_2$	0.878	0.645	0.417

* The numbers in brackets indicate the position of atoms of C and N in the molecule as given in their formulae based on crystallographic analysis (Vol. I, 181; II, 372, 385).

The relative change δ from ΔC^o to ΔC^x can be expressed by equation (22)

$$\delta = \frac{100\,(\Delta C^x - \Delta C^o)}{\Delta C^o} \tag{22}$$

Delpuech and Cherville [45b] suggest using values of $\Delta C^x/l$ and δ as data indicating the tendency of explosives to decompose under impact. This would be particularly advisable with new explosives which although their structure is known, possess unknown properties.

While examining the shape of the curve of the sensitivity to impact of TNT at different temperatures (Vol. I, p. 320, Fig. 74). T. Urbański [48] advanced an hypothesis that the increase of sensitivity is due to the increase of entropy (S) and therefore decrease of free energy $G = H-TS$. A critical change is at the melting point of TNT – *ca.* 80°C which is well known, is manifested by a rapid increase of entropy (Fig. 2). Cruchaud [79] drew attention to the electric phenomena which accompany the shock and friction produced by the impact. Charging with static electricity is an important factor influencing the explosion according to this author.

Attention is drawn to two monographs dealing with the initiation of explosives by impact: solid explosives by Afanasyev and Bobolev [49] and liquid by Dubovik and Bobolev [50]. The authors based their views on the considerable

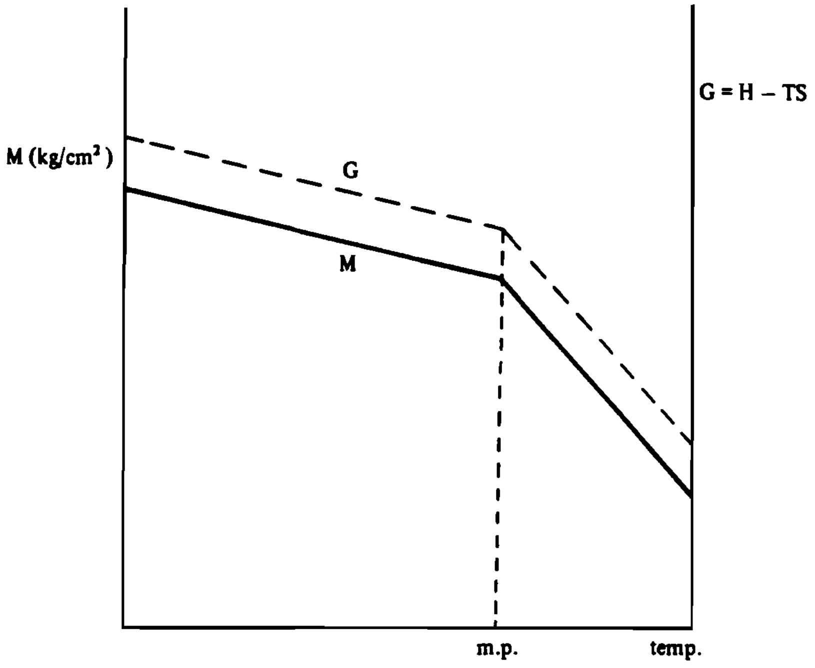

FIG. 2. Sensitivity to impact of TNT (*M*) and Gibbs free energy (*G*) as a function of temperature. Melting point: m.p. (According to T. Urbański [48]).

work carried out by Khariton, Andreev, Belyaev, Kholevo, Sukhikh, Avanesov, Bolkhovitinov, Baum and their own experiments. The authors agree with the thermal nature of the sensitivity of explosives to impact. However most of the problems raised by the authors of the monographs are outside the scope of the present book.

Sensitivity of high explosives (*HE*) *to initiation* by an initiating explosive ('gap sensitivity', 'initiability') is less defined than the sensitivity to impact and cannot be expressed in absolute units. The sensitivity of *HE* to initiation is usually determined:

(1) by the amount of the initiating explosive in the detonator (this method is also used to determine the 'initiating strength' of primary explosives),

(2) by transmitting the detonation from one charge to another through air or other medium (water or a sheet of metal or a polymer) of different thickness,

(3) by determining the critical diameter, that is the minimum diameter which is able to transmit the detonation.

It is well known that the *HE* can be arranged in the sense of decreasing sensitivity to detonation: *O*-nitro, *N*-nitro and *C*-nitro compounds.

Cachia and Whitbread [63] described a 'gap' test of different explosives and determined the minimum gap thickness that inhibits detonation.

Recently Ahrens [64] reviewed the problem of determination of the sensitiveness of explosives to initiation.

Sensitivity to friction is also less defined than the sensitivity to impact and can be expressed only by figures comparative to a standard. By decreasing sensitivity the explosives can be arranged as follows [65]:

initiating explosives (with exclusion of azides),
O-nitro compounds,
N-nitro compounds and metal azides,
C-nitro compounds.

The sensitivity of explosives to heating, naked flame, impact and friction is decisive in the international rules for railway traffic 'RID' (Règlement International Concernant le Transport des Marchandises Dangereuses) [65]. Analogous rules 'ADR' are concerned with international motor traffic [66].

Important reviews have appeared on the sensitivity and initiation of explosives [67, 68].

Action of Ultrasonic Waves and Laser Pulse

Early work on the action of ultrasonic waves on explosives indicated that such sensitive substances as nitrogen iodide could explode [73, 74] but that silver fulminate could not be brought to detonation [74].

Some experiments by Wolfke [69] have shown that high intensity waves were required to bring mercury fulminate to detonation. Negative results were obtained by Renaud [75] who pointed out that the positive results of Marinesco [74] were due to the mechanical action of pushing crystals by the oscillator. This query was recently solved by Leiber [76] who stated that the detonation of nitroglycerine by ultrasonic waves can occur provided that the explosive contains bubbles and the nature of the effect is mainly thermal bringing the temperature to 300–500°C through the adiabatic pressure of the order of 33 bar.

Mizushima and Nishiyama [77] examined the action of laser and found that compressed explosives can be brought to decomposition by a giant laser pulse. Loose explosives cannot detonate. They examined initiating explosives, PETN, RDX, TNT and Tetryl.

Action of Irradiation

Numerous publications particularly in recent years have been dedicated to the sensitivity of explosives to various forms of irradiation.

Bowden and Yoffe [70] reviewed the literature and their own work on the decomposition of initiating explosives by irradiation with electrons, neutrons, fission products, α-particles, X-rays and γ-rays.

Recently two abundant reviews appeared in the *Encyclopedia of Explosives* edited by Kaye and Herman [71, 72].

Thus Avrami [71] reviewed radiation effects on explosives, propellants and pyrotechnics. Here are some of the main conclusions taken from the work of Avrami and numerous authors: initiating explosives are decomposed under irradiation with α-particles, neutrons, γ-radiation, electron irradiation and underground testing. Among the reviewed papers Avrami reported his own work on the influence of Co^{60} gamma radiation on the detonation velocity of explosives: they all show a fall in velocity after irradiation. Cyclonite (EDX) appears to be particularly sensitive, less sensitive are PETN and HMX. Aromatic compounds such as TNT and Tetryl seem to be still less sensitive.

A good stability is shown by heat resistant explosives: TACOT, DATB (Diaminotrinitro-) and TATB (Triaminotrinitrobenzene) (Chapter VII).

Helf [72] described the technique of radiation gauging in energetic materials.

A remarkable paper has been published by Cherville and co-workers [80]. They examined the behaviour of a few secondary explosives to the irradiation from Co^{60} and introduced the value G_{NO_2}: the quantity of NO_2 by irradiation. They found the values of G_{NO_2} being correlated to the ability of explosives to detonate. The following are the figures for G_{NO_2}:

PETN	3.80
Hexogene, Cyclonite (RDX)	0.90
Octogene (HMX)	0.80
Tetryl	0.006
Picric acid	0.001
TNT	0.001
Nitroguanidine	0

Influence of High Temperature

The behaviour (including the decomposition) of explosives at high temperature is one of their important characteristics. With the advent of DSC (differential scanning calorimeter) high precision can be reached of the examination of endo- and exothermic changes in substances with the increase of temperature. This was reviewed by Collins and Haws [81]. The pioneering work on DSC by Tucholski in 1932–33 [82] should be recalled (see also Vol. I, p. 525).

Two Soviet monographs appeared [83, 84] both dedicated to thermal decomposition and burning of explosives, and a review by Maycock [85].

INCREASING THE STRENGTH OF EXPLOSIVES BY ADDING METALS

A popular method of increasing the strength of explosives is by adding aluminium and less frequently calcium silicide, ferro-silicon, silicon (Vol. III, p. 266).

The following figures illustrate the action of aluminium on the calorific value of RDX (Cyclonite) given by Belaev [86]:

RDX + Al	0% Al	cal. val.	1200 kcal/kg
	5%		1380
	10		1420
	15		1520
	20		1690
	33		1890

Recently the addition of Boron or its compound with hydrogen, for example, 'ortho-borane' ($C_2H_{12}B_{10}$) was investigated by Pepekin, Makhov and Apin [87]. They examined mixtures of PETN and Cyclonite with boron or ortho-borane. The calorific value of Cyclonite–Boron reached a maximum (1890 kcal/kg) with *ca.* 16% B. PETN with *ca.* 22% reached a value of *ca.* 2050 kcal/kg.

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CHAPTER 1

NITRATION AND NITRATING AGENTS

(Vol. I, p. 4)

A considerable number of papers were dedicated to the problem of nitration in the years following the publication of Vol. I.

Among nitrating agents the most important still remain nitric acid–sulphuric acid mixtures, but some other very efficient nitrating agents related to nitric acid have been found and are in use, mainly on a laboratory scale.

NITRIC ACID (Vol. I, p. 6)

Considerable attention is currently being paid to nitric acid (and nitrogen dioxide) because of their wide use, not only for nitration, but also as oxidizing agents in rocket propellant systems. A review has recently been published by Addison [1].

Pure nitric acid free of nitrogen dioxide, so called white fuming nitric acid (WFNA), is in use as an oxidizer and for nitration of some compounds (e.g. hexamethylene tetramine [hexamine], Vol. III, p. 87).

However WFNA is relatively unstable and with time develops a certain amount of dinitrogen tetroxide. More stable for rocket propulsion is red fuming nitric acid (RFNA) which contains *ca.* 14 wt% N_2O_4. It is formed from WFNA or from nitric acid with added N_2O_4. RFNA is the equilibrium product formed from both extremes of the concentration range:

$$\underset{\text{WFNA}}{HNO_3} \longrightarrow \underbrace{\underset{84.5\%}{HNO_3} + \underset{14\%}{N_2O_4} + \underset{1.5\%}{H_2O}}_{\text{RFNA}} \longleftarrow HNO_3 + \underset{\substack{\text{(in excess,}\\ \text{subject to}\\ \text{evaporation).}}}{N_2O_4} \tag{1}$$

RFNA is more reactive than WFNA, N_2O_4 being a *sui generis* catalyst of the oxidation reactions. Subsequently RFNA is more recommended in rocket fuel than WFNA, but should be avoided in most nitration reactions. Dinitrogen tetroxide (usually given in analytical data as NO_2) is present in spent acids containing nitric and sulphuric acids and is formed in the course of nitration as a result of the oxidation of the nitrated substances. The content of NO_2 in the spent acid can be as high as 5%. Commercial 'fuming nitric acid' ('anhydrous nitric acid') usually contains less than 1% NO_2 and is used for the nitration of hexamine.

Pure nitric acid (WFNA) can be obtained by distillation of nitric acid from a mixture of concentrated nitric acid (d 1.50 at 25°C) and concentrated sulphuric acid, under reduced pressure at room temperature. A white crystalline solid results with the following properties [1]:

m.p. $-$ 41.6°C
b.p. $+$ 82.6°C
d $-$ 1.549 at 0°C
viscosity 10.92 cP at 0°C
dielectric constant 50 ± 10 at 14°C
surface tension 43.5 dy/cm at 0°C
specific conductivity 3.77×10^{-2} ohm^{-1} cm^{-1}.

The latter two figures are high due to hydrogen bonding (Vol. I, p. 7, Fig. 1).

The data in Fig. 1a (Vol. I, p. 7) should be slightly altered on the basis of more recent measurements by micro-wave spectroscopy [2, 3]. They are now given in Fig. 3.

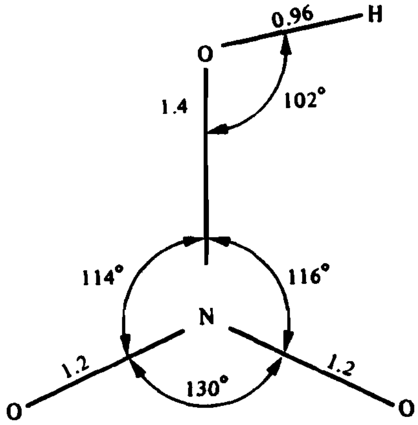


FIG. 3. Structure of the molecule of nitric acid [2, 3].

It is well known that nitric acid forms an azeotropic solution with water. It contains 68.5 wt% HNO_3 and boils at 122°C under standard atmospheric pressure.

Cryoscopic measurements (Vol. I, pp. 15–16) have shown that only a little over 3% of pure nitric acid is dissociated at -40°C according to the equation:

$$\underset{}{2HNO_3} \rightleftharpoons \underset{1.2}{NO_2^+} + \underset{1.7}{NO_3^-} + \underset{0.5\ \text{wt\%.}}{H_2O} \tag{2}$$

Water is in the form of the nitric acid hydrate.

A few more spectroscopic data for nitric acid should be added to those previously given (Vol. I, p. 22). Vitse [31d] has found bands in nitric acid: 1680, 1300 and 930 cm^{-1} assigned to NO_2 and band 3200 cm^{-1} to OH stretching vibrations.

It is now generally accepted that the nitronium ion NO_2^+ is the main nitrating agent. Although most industrial nitrations are carried out by nitric acid–sulphuric acid mixtures, some compounds can be nitrated with nitric acid alone (production of tetryl, Vol. III, p. 42). Some products, such as PETN (Vol. II, p. 185) are usually obtained by nitration with nitric acid alone and Cyclonite (if made by nitration) is produced exclusively with nitric acid free of N_2O_4 (Vol. III, p. 87).

Although the nitronium ion is the nitrating agent, there are known examples when nitration can occur in media in which the concentration of NO_2^+ is too small to be detected spectroscopically (Vol. I, pp. 25, 48). This was pointed out by Bunton and Halevi [4] who succeeded in nitrating aromatic compounds with 40–60% aqueous nitric acid. Bunton and co-workers [5, 6] showed that the nitronium ion was an intermediate in both oxygen-exchange and aromatic nitration in the sense of reactions:

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-, \tag{3}$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O. \tag{4}$$

Hydrated nitronium ion (nitracidium ion) $H_2NO_3^+$ is a source of the nitrating agent NO_2^+.

It was reported [7] that nitration of 1,5-dinitro-naphthalene can occur with 70% nitric acid to yield trinitro-naphthalenes.

The problem of nitration with aqueous nitric acid was reviewed by Hanson and associates [8]. They confirmed the idea of nitracidium ion being a nitrating agent and pointed out that attention should be paid to the presence of nitrous acid in the system, as nitration with dilate nitric acid can proceed through the nitrosation by nitrous acid formed as the result of oxidation–reduction. T. Urbański and Kutkiewicz [9] (Vol. I, p. 85) found that 8-hydroxyquinoline can be nitrated by boiling with 0.5% nitric acid to yield 5,7-dinitro-8-hydroxyquinoline. It was also found that 8-hydroxy-5-nitroquinoline yielded the same dinitro derivative.

As far as the mononitration of phenol and the formation of 8-hydroxy-5-nitroquinoline can be explained in terms of the conventional mechanism of nitrosation followed by the oxidation of nitroso to the nitro group (p. 23), this mechanism could not explain the formation 5,7-dinitro-8-hydroxyquinoline from mononitro compound. The mononitrophenols cannot be nitrosated with nitrous acid and subsequently the formation of the second nitro group cannot occur through nitrosation. Nevertheless, the reaction of formation of the dinitro compound from the mononitro product is preceded by the oxidation and evolution of NO_2. This would apparently suggest that nitrosation (as shown above) is not possible with 8-hydroxy-5-nitroquinoline.

Also Ross and co-workers [87] pointed out that the accepted scheme of nitration of phenol in 56.2% sulphuric acid through nitrosation prior to nitration, is inconsistent with the results and expressed the view that another route should exist.

The author of the present book suggests the solution of the problem of nitration of phenols with dilute nitric acid in a two-fold way:

(1) Through oxidation (which always accompanies nitration and particularly the nitration of phenols) NO_2 is evolved and the well known reaction occurs:

$$2\,NO_2 + H_2O \longrightarrow HNO_3 + HNO_2. \tag{5a}$$

(2) The dilute nitric acid originally present in the solution and also formed in reaction (5a) can given rise to NO_2^+ in a readily oxidizable medium according to scheme (5b) rationalized by the author [112]:

$$NO_3^- \longrightarrow NO_2^+ + O^{2-} \tag{5b}$$

Reaction (5b) can take place in readily oxidizable mediums such as phenols and aromatic amines.

Usanovich [128] has drawn attention to the amphoterism of HNO_3 which, to follow ideas of Hantzsch (Vol. 1, p. 12) HNO_3 is a base when interacting with H_2SO_4. Usanovich and his associates found that HNO_3 is a base towards CCl_3COOH but an acid towards $CH_3CO\ OH$. With the amphoteric behaviour of HNO_3 the dilution of nitric acid with such substances as (H_2SO_4, H_3PO_4) toward which HNO_3 is a base or which (H_2O, CH_3COOH) act as bases toward HNO_3 promotes or hinders the nitration of aromatic compounds respectively.

NITRIC AND SULPHURIC ACID

Mixtures of nitric and sulphuric acids contain nitronium sulphates which have been described by Ingold and associates, Woolf and Emeléus (Vol. I, p. 19). Revallier and co-workers [10] have found by Raman spectroscopy and vapour pressure measurements, that compounds made by acting with SO_3 on nitric acid are salts of nitronium ion (NO_2^+) and sulphate anions. Vitse [11] established the structure of the compound $N_2O_5.4SO_3$ as nitronium ion salt by X-ray crystallography. The salts of pyrosulphuric acid (Vol. I, p. 12) can be present only in a mixture of nitric acid with oleum or SO_3. They are described in the paragraph on nitronium salts (p. 27). The presence of NO_2^+ in various solutions was discussed in Vol. I, pp. 14–49.

The basicity of nitric acid in the sense of the dissociation $NO_2OH \rightleftharpoons NO_2^+ + OH^-$ in concentrated sulphuric acid was recently studied by Marziano *et al.* [12]: the ionization ratio NO_2^+/HNO_3 of nitric and 80–96% sulphuric acids has been evaluated by Raman and ultraviolet spectroscopy. The function pK_a of nitric acid as a base was calculated $pK_a = -15.2$.

As far as the activity of the nitrating mixture (Vol. I, p. 29) is concerned, a novel approach to the problem was recently developed by Marziano and associates [13]. In a series of papers on thermodynamic analysis of nitric acid with sulphuric or perchloric acid these authors introduced a new function of the activity coefficient M_C:

$$M_C = \log \frac{f_B f_{H^+}}{F_{BH^+}}$$

where f_B is the activity coefficient of the nitrated substance, f_{H^+} activity coefficient of the proton H^+.

Effects of Adding Salts on Nitration in Sulphuric Acid

A few authors have examined the effect of adding salts on the rate of nitration in sulphuric acid.

Thus Surfleet and Wyatt [14] studied the nitration of benzenesulphonic acid in sulphuric acid and found that the addition of hydrogen sulphates of various metals increases the nitration rate. The most marked effect occurred with calcium and barium hydrogen sulphates. An explanation of the effect was sought in terms of the Brönsted salt-effect theory. It was suggested that the main influence of ionic solutes is in the activity coefficient of the nitrated substance (f_B) since the activity coefficients of the other two species, the nitronium ion ($f_{NO_2^+}$) and the similarly charged transition complex ($f_+^{\ddagger}$) as a ratio in the Brönsted equation and would be approximately equally affected by changes in the ionic environment. The view was expressed that reactions involving only ionic species would exhibit small salt effects.

Bonner and Brown [15] expressed the view that the increase in reaction rate due to added salts is similar to the increase initially resulting from the addition of water to anhydrous sulphuric acid, attaining the maximum at *ca.* 90% acid. They supported it by examining the rates of nitration of trimethylphenylammonium ion and 1-chloro-4-nitrobenzene. When ammonium sulphate was added, the rate increased more than ×20 their value in the anhydrous acid. On the nitration of cellulose with nitric acid in the presence of inorganic salts (see Vol. II, p. 346).

Nitric Acid and Trifluoromethane Sulphonic Acid

A very interesting nitrating mixture has been reported by Coon, Blucher and Hill [16]. It was composed of nitric acid and trifluoromethane sulphonic acid: $CF_3.SO_3H$. It contains nitronium salt: NO_2^+ $CF_3SO_3^-$. The major difference between the aromatic nitration with this and other nitronium salt is an extremely high reaction rate.

The nitration of toluene with such a mixture is described in the chapter dedicated to the nitration of aromatic hydrocarbons.

Nitric Acid and Hydrofluoric Acid

NMR spectroscopy revealed [17] that NO_2^+ is also formed by acting with HF on nitric acid, viz.:

$$HNO_3 + 2HF \longrightarrow NO_2^+ + H_3O^- + 2F^- . \tag{6}$$

Earlier the presence of NO_2^+ in nitric acid–hydrofluoric acid solution was postulated by Vorozhtsov Jr and his School [18]. Vorozhtsov Jr and associates [19] found that nitric acid–hydrofluoric acid solution can produce both: the nitration and fluorization of aromatic compounds through an ipso-attack (see p. 50) of both NO_2^+ and F^-.

Nitric and Phosphoric Acid

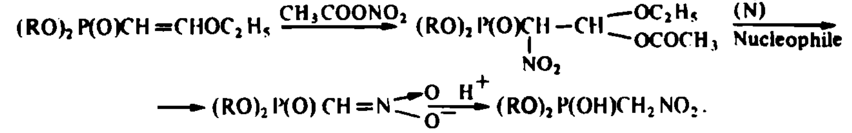
It is admitted that anhydrous solution of nitric and phosphoric acids contains nitronium ion.

So far nitric–phosphoric acid mixtures have been mainly of theoretical interest (Vol. II, p. 341). However recently a few attempts have been reported on the nitration of toluene with nitric–phosphoric acid mixtures in order to reduce the proportion of *o*-nitrotoluene and subsequently to increase the yield of para isomer (Harris [20]).

Nitric Acid and Acetic Anhydride

Nitric acid and acetic anhydride mixture is often used as a nitrating agent on a laboratory scale. It is possible that nitronium ion is present in such solutions [21]. According to A. Fischer and associates [22, 23] nitric acid–acetic anhydride mixtures contain nitronium acetate. Nitric acid–acetic anhydride yield not only nitro compounds but can also produce an acetylation through the oxidation and subsequent acetylation of the side chain [23]. Thus *o*-xylene subjected to the action of nitric acid–acetic anhydride at 0°C gave 16% 3-nitro- and 33% 4-nitroxylene and 51% 3,4-dimethylphenyl acetate. The authors suggested it as being the result of the presence of oxonium ion $CH_3COO^+NO_2$. Nucleophilic attack on a ring carbon leads to acetoxylation.

Very often nitration with nitric acid–acetic anhydride solution is referred to as nitration with acetyl nitrate (Vol. I, p. 44). Petrov and co-workers [24] experimented with nitric acid and acetic anhydride with a small quantity of sulphuric acid at 35°C on ethoxyvinylphosphates. The ester was hydrolysed to yield a nitromethane derivative:



$$(RO)_2P(O)CH{=}CHOC_2H_5 \xrightarrow{CH_3COONO_2} (RO)_2P(O)\underset{\substack{|\\ NO_2}}{C}H{-}CH\begin{smallmatrix}OC_2H_5\\ OCOCH_3\end{smallmatrix} \xrightarrow[\text{Nucleophile}]{(\ddot{N})} \qquad (7)$$

$$\longrightarrow (RO)_2P(O)CH{=}N\begin{smallmatrix}O\\ O^-\end{smallmatrix} \xrightarrow{H^+} (RO)_2P(OH)CH_2NO_2.$$

Literature on the practical use of nitric acid–acetic anhydride includes also some warnings on explosion hazards associated with the use of mixtures of fuming (97%) nitric acid with acetic anhydride. Thus Brown and Watt [25] demonstrated that mixtures of nitric acid with acetic anhydride containing more than 50% by weight of nitric acid can undergo a spontaneous explosion.

Dingle and Pryde [26] extended this warning also to mixtures containing less than 50% nitric acid. Particularly dangerous is the addition of a small quantity of water or some mineral acids to such a mixture. A mixture containing 6% nitric acid in acetic anhydride with 1.7% concentrated hydrochloric acid was found to self-heat at 20°C and to fume-off vigorously at 60°C with gas evolution.

Nitric Acid with Cerium Ammonium Nitrate or Tallium Nitrate

Considerable interest has been shown recently in the use of cerium (IV) salts as oxidizing agents. Cerium (IV) ammonium nitrate can also be a nitrating agent [125]. It can also act in the presence of acetic acid [119]. In the presence of nitric acid [120] it can form nitrate esters from the methyl group, viz.:

$$-CH_3 \longrightarrow -CH_2ONO_2$$

(see Chapter X).

Tallium (III) nitrate can also be used as a nitrating agent [119].

NITRONIUM CATION (NO_2^+) AND ITS SALTS

Crystalline nitronium salts were first obtained as early as 1871 by Weber [27] (see also Vol. I, p. 12). He gave the composition $N_2O_5.4SO_3.3H_2O$ and $N_2O_5.4SO_3.H_2O$. Several similar salts have been obtained by a number of authors [10, 28–30]. The most important contribution to the knowledge of stoichiometry of $N_2O_5.SO_3$ and $N_2O_5.SO_3.H_2O$ complex-salts has been made by Vitse [31].

All these salts possess ionic structure comprising cation NO_2^+ bonded in various proportions to HSO_4^-, $HS_2O_7^-$, $S_2O_7^{2-}$ etc.

Some of the salts possess a great stability if protected from moisture. Thus Werner compound $N_2O_5.4SO_3.H_2O$ has the structure NO_2^+ $HS_2O_7^-$ and m.p. 105.6°C [10a]. The compound $8N_2O_5.20SO_3.7H_2O$ with the structure $(NO_2^+)_{16}S_2O_7^{2-}(HS_2O_7^-)_4(HSO_4^-)_{10}$ has m.p. 119.8°C. Its crystal structure was determined by X-ray analysis [11] as already mentioned (p. 28).

Other salts of nitronium ion and sulphuric acid have been previously described (Vol. I, p. 19). Ingold and co-workers (Vol. I, p. 19) obtained crystalline nitronium perchlorate which was relatively stable, but decomposed on storage and was not further investigated.

R. J. Thomas, Anzilotti and Hennion [32] reported that boron trifluoride could play the same part as sulphuric acid in the nitration of aromatics. Olah and co-workers [33, 40] prepared and successfully applied a number of stable salts of nitronium ion in a relatively simple way:

$$NO_2^+ X \text{ where } X = BF_4, AsF_6, PF_6$$

and

$$(NO_2^+)_2 Y \text{ when } Y = SiF_6^{2-}.$$

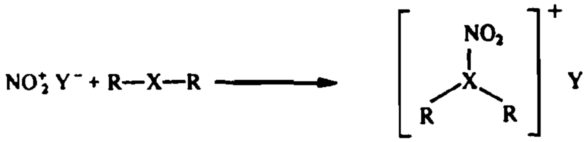
Particularly important is nitronium tetrafluoroborate obtained by adding anhydrous HF to nitric acid in a solvent such as nitromethane or methylene chloride and then saturating the solution with boron trifluoride (8):

$$HNO_3 + HF + 2BF_3 \longrightarrow NO_2^+BF_4^- + BF_3.H_2O. \tag{8}$$

An almost quantitative yield of stable nitronium salts $NO_2^+BF_4^-$ can be obtained in that way [34] and it is now commercially available [35]. It is a colourless, crystalline very stable compound which decomposes above 170°C into NO_2F and BF_3 without subliming. It is a very strong nitrating agent [36].

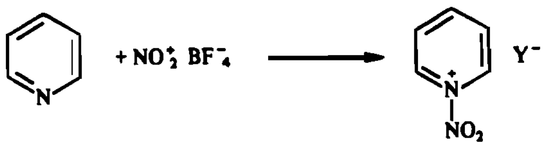
Among other compounds nitric acid–boron trifluoride $HNO_3.2BF_3$ complex (m.p. 53°C) obtained by Revallier and associates [37] proved by Raman spectroscopy to possess the structure of nitronium salt NO_2^+ $(BF_3)_2OH^-$ [38].

Nitronium ion is able to form nitroxonium and pyridinium ions with ethers and pyridine or collidine respectively by acting on ethers and pyridine or collidine respectively with nitronium tetrafluoroborate [39, 40d]:



(9)

$Y = PF_6^-, BF_4^-$
$X = O, S; R = \text{Alkyl}, H$



(10)

The nitroxonium and nitropyridinium (or nitrocollidinium) ions are efficient nitrating agents. They also can form *O*-nitro compounds.

Nitronium hexafluorophosphate ($NO_2^+ PF_6^-$) is also a strong nitrating agent according to Olah and Lin [40b]. It can nitrate alkanes at 25°C to a small yield of nitro compounds (2–5% for ethane to butane). Nitronium tetrafluoroborate in fluorosulphuric acid (FSO_3H) possesses strong nitrating properties. It can nitrate *m*-dinitrobenzene to *sym*-trinitrobenzene with a yield of 66% [40c].

Among the salts of nitronium ions a very active nitrating agent is nitronium trifluoromethyl sulphate ($NO_2^+ CF_3SO_3^-$) as already mentioned [16].

Nagakura and Tanaka [41] explained a great reactivity of NO_2^+ by calculating its lowest vacant orbital and the highest occupied orbital of benzene. The figures are −11.0 and −9.24 eV respectively. Other electrophilic reagents, such as Br^+ and Cl^+ are less reactive. They gave values of −11.8 and −13.0 eV respectively.

Nitronium salts are usually applied in an aprotic solvent [35]. Such is tetramethylene sulphone ('Sulfolan') used by Olah [40]. However, Giaccio and Marcus [42] suggested acetic acid as a solvent. This, however, reacts with nitronium tetrafluoroborate on standing at room temperature to yield acetyl nitrate:

$$CH_3COOH + NO_2^+BF_4^- \rightleftharpoons CH_3COONO_2 + HF + BF_3. \tag{11}$$

The nitrating action of acetyl nitrate differs from that of nitronium tetrafluoroborate [40]. Also the stability of acetyl nitrate is not satisfactory.

Dinitrogen Pentoxide (N_2O_5) (Vol. I, p. 105)

Dinitrogen pentoxide (nitric anhydride) can be a source of the nitronium ion. As previously mentioned Titov suggested (Vol. I, p. 106) that dinitrogen pentoxide undergoes a heterolytic dissociation:

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-. \tag{12}$$

The infra-red bands of the ionic form at liquid nitrogen temperature have been examined by Teranishi and Decius [43] and substantiated by Hisatsune and co-workers [44] who also examined Raman spectra. They found a temperature dependence of the structure of solid N_2O_5 which changed the covalent structure $O_2N-O-NO_2$ into ionic at temperatures from −175° to −80°C.

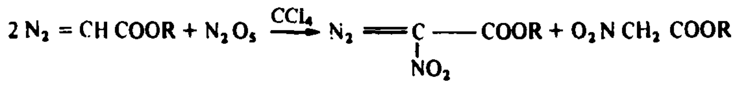
The covalent structure is characterized by a bent of the central N—O—N group.

Dinitrogen pentoxide readily forms nitronium salts. As mentioned, Weber [27] and other authors [28–31] obtained a number of sulphates of NO_2^+. Bachman and Dever [45] prepared a complex with BF_3 which most likely possesses the structure $NO_2^+\ BF_3ONO_2^-$. Kuhn and Olah [33] obtained nitronium tetrafluoroborate by adding anhydrous HF as a solvent to N_2O_5 and BF_3:

$$N_2O_5 + HF + BF_3 \longrightarrow NO_2^+\ BF_4^- + HNO_3. \qquad (13)$$

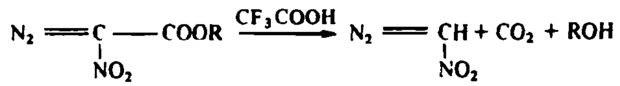
T. Urbański used N_2O_5 in vapour phase or in a solution in nitric acid to nitrate cellulose (Vol. II, p. 348) and starch (Vol. II, p. 430).

N_2O_5 was successfully used by Schöllkopf and associates [46] to nitrate aliphatic diazocompounds to obtain eventually nitrodiazomethane [46b] and dinitrodiazomethane [46c]. As the first step esters of diazoacetic acid were nitrated with half a mole of N_2O_5 in carbon tetrachloride at −20 to 30°C:



$$2\,N_2{=}CH\,COOR + N_2O_5 \xrightarrow{CCl_4} N_2{=}\underset{NO_2}{\underset{|}{C}}{-}COOR + O_2N\,CH_2\,COOR$$

$$(R = C_2H_5 \text{ or ter–}C_4H_9) \qquad (14)$$

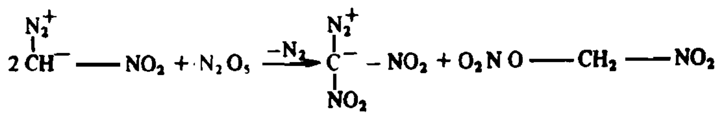


$$\underset{\text{I}}{N_2{=}\underset{NO_2}{\underset{|}{C}}{-}COOR} \xrightarrow{CF_3COOH} \underset{\text{II}}{N_2{=}\underset{NO_2}{\underset{|}{C}}H} + CO_2 + ROH$$

I II

Nitrodiazoester (I) is relatively acid-stable, but the COOR group can be cleaved off by acting with trifluoroacetic acid in ether to obtain nitrodiazomethane (II) $O_2N{-}CH\ N_2^+$ m.p. 55°C. It is a substance which is sensitive to impact and explodes on heating.

Nitrodiazomethane was nitrated [46c] with N_2O_5 in dichloromethane at −30°C to yield dinitrodiazomethane (III) and a nitromethyl nitrate ester (IV)



$$2\,\overset{N_2^+}{\overset{|}{C}}H^- {-}NO_2 + N_2O_5 \xrightarrow{-N_2} \underset{NO_2}{\underset{|}{\overset{N_2^+}{\overset{|}{C}}}}{}^- - NO_2 + O_2NO{-}CH_2{-}NO_2 \qquad (15)$$

III IV

III is an explosive substance with m.p. 65°C (with decomposition).

N_2O_5 possesses marked oxidizing properties [47]: a small yield of CO_2 was formed by acting with N_2O_5 on CO. Baryshnikova and Titov [123] have found an interesting reaction of N_2O_5 on aromatic compounds which consists in both nitration and oxidation. Thus chlorobenzene was transformed into chloronitrophenols.

Dinitrogen Tetroxide and Nitrogen Dioxide (Vol. I, p. 90)

The increasing importance of dinitrogen tetroxide brought to light a number of new facts on the properties of the substance.

Some physical constants are [1]:

freezing point −11.2°C
b.p. 21.15°C
density 1.470–1.515 g/cm^3 between +10° and −10°C
viscosity 0.468–0.599 cP between +10° and −10°C
dielectric constant 2.42
surface tension 26.5 dyn/cm at 20°C
specific conductivity 10^{-12} ohm^{-1} cm^{-1}.

An extensive review of the properties of dinitrogen tetroxide has been given by Riebsomer [47]. The addition of N_2O_4 to olefins was reviewed by Shechter [48] and free radical reactions of NO_2 by Sosnovsky [48a].

The N—N bond in dinitrogen tetroxide can readily be split above room temperature. The case of breaking N—N bond is due to its low enthalpy: $-\Delta H$ of N—N in N_2O_4 is 14.6 kcal/mol and similarly in N_2O_3 is 10.2 kcal/mol. [49].

The N—N bond is mainly σ in nature, not of pure π character according to Green and Linnett [50]. This was based on a calculation by LCAO MO method and was contradictory to earlier views. The bond N—N seems to be of an unusual kind, not fully understood, as the two NO_2 units do not rotate with respect to each other in spite of the length of the bond.

The views of Green and Linnett were subjected to criticism by R. D. Brown and Harcourt [113]. The latter pointed out that Green and Linnett had overlooked the significant effect of σ-electron delocalization upon N—N and N—C bonds. Brown and Harcourt proposed a new electronic structure with '$\sigma + \pi$' model.

A review recently appeared [126] on the spectrum of NO_2 in gas phase. The spectrum is rich and complex and was examined by modern techniques. The study is outside the scope of the present book.

N_2O_4 is miscible with many organic liquids and is a solvent of many solid organic substances.

Ammonium nitrate is insoluble in N_2O_4 but alkylammonium nitrates dissolve readily [1].

Nitrogen dioxide at high temperature (*ca.* 620°C) was subjected to homolytic dissociation into nitric oxide and oxygen atom. The same occurred upon irradiation with 313 and 316 nm light [51, 52].

The heterolytic dissociation can be represented in two ways:

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \tag{16}$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \tag{17}$$

and there is also an irreversible heterolytic oxygen exchange:

$$NO_2^+ + NO_2^- \longrightarrow NO^+ + NO_3^-. \tag{18}$$

However the species NO_2^+ and NO_2^- have not been identified as free ions in liquid N_2O_4. They exist as the ion pair $[NO_2^+ NO_2^-]$. In the presence of an electron-pair acceptor, complexes are formed which contain the nitronium ion. This happens in the presence of Lewis acid halides used for the first time ($AlCl_3$) by Schaarschmid (Vol. I, p. 103). Boron trifluoride reacts with N_2O_4 to form $N_2O_4.BF_3$ [53, 54] and $N_2O_4.2BF_3$. Their structures were suggested as being $NO_2^+ BF_3NO_2^-$ and $NO_2^+ [N(OBF_3)_2]^-$ respectively. These complexes possess only a moderate nitrating ability, a fact which casts some doubt on whether they possess the structure with nitronium ion. It is known that N_2O_4 in nitric acid is almost fully ionized into NO^+ and NO_3^-. In view of the absence of NO_2^+ the complex $N_2O_4.BF_3$ may have the structure of a nitrosonium salt $NO^+ BF_3NO_3^-$. Indeed it shows an ability to nitrosate and to diazotize [53] and spectroscopic examination [56] showed only a relatively weak band at 1400 cm^{-1} and a strong one at *ca.* 2340 cm^{-1}.

It is suggested [40] that an equilibrium exists between nitronium and nitrosonium forms of the complex $N_2O_4.BF_3$ i.e.

$$NO_2^+ [BF_3\,NO_2]^- \longrightarrow NO^+ [BF_3NO_3]^- \tag{19}$$

A solution N_2O_4 + HF should be considered as a potential nitrating agent [57].

Dinitrogen tetroxide can give additional complexes with compounds possessing an ether bond. They were examined by Shechter *et al.* and described in his review paper [48].

Here are the most important of the compounds:

1.	$2(C_2H_5)_2O \cdot N_2O_4$	m.p. −74.8°C
2.	$2(C_5H_{10}O) \cdot N_2O_4$ (Tetrahydropyren)	m.p. −56.8°C
3.	$C_4H_8O \cdot N_2O_4$	m.p. −20.5°C
	$2C_4H_8O \cdot N_2O_4$ (Tetrahydrofurane)	m.p. (indefinite)
4.	$O(CH_2CH_2)_2O \cdot N_2O_4$	m.p. +45.2°C

Davies and C. B. Thomas [58] reported an interesting instance of nitration of arylthallium (III) aromatic complexes with nitrogen dioxide at room temperature. Tallium (III) fluoroacetate was used as the agent metallating an aromatic ring which can react with NO_2:

$$\mathrm{Alk\ C_6H_5\ Tl(OOCCF_3)_2} \xrightarrow{NO_2} \mathrm{Alk\ C_6H_4NO_2}. \tag{20}$$

A remarkable feature of the reaction is the high proportion of *p*-nitro products. More details are given in the chapter on the nitration of toluene.

Dinitrogen tetroxide in vapour phase can be used as an energetic nitrating agent (Vol. I, pp. 92–105). The nitration of aromatics can be facilitated by irradiation with ultraviolet light. The claim of Gorislavets (Vol. I, p. 105) was substantiated by Bunbury [59].

As far as nitration with liquid N_2O_4 is concerned, attention should be paid to the danger of keeping solutions of alkanes with N_2O_4.

T. Urbański and Falęcki [60] reported a spontaneous explosion when a solution of N_2O_4 in *n*-alkanes was kept for a few days at room temperature. This was most likely a consequence of the formation of branched reaction chains through free radicals.

In addition to the use of dinitrogen tetroxide as an oxidizer in rocket propellant systems, and as a potential nitrating agent is is also used as a cooling liquid in nuclear energy reactors under the name of 'Nitrin' [61].

Dinitrogen Tetroxide–Nitric Acid

The two liquids: HNO_3 and N_2O_4 are not miscible in all proportions. At room temperature (20°C) an immiscibility region extends between *ca.* 54 and 92 wt% of N_2O_4. The critical solution temperature is 60.9°C at a composition 68.2 wt% N_2O_4. The phase diagram is shown in Fig. 4 [62, 63].

A solid compound $(HNO_3)_2\,N_2O_4$ exists, it contains 42.2% N_2O_4. It gives an eutectic m.p. −65°C at 25.6% N_2O_4 [64]. The compound gives maximum values of density and viscosity [65]. Spectroscopic examination shows [1] that the species present in HNO_3–N_2O_4 mixtures are as follows:

$$NO^+,\ NO_2^+,\ NO_3^-,\ H_2O,\ HNO_3,\ NO_2,\ N_2O_4.$$

The mixtures HNO_3–N_2O_4 are highly corrosive and attack metals (steel, aluminium or chromium, nickel). Corrosion can be inhibited by the addition of fluorine compounds, notably HF or PF_6 [1]. The addition of 0.7 wt% of HF reduces the corrosion by a factor over 100 and the mixture of 44% N_2O_4 and 56% HNO_3 with 0.7–1.0% HF termed 'standard HDA' is in current use as a rocket oxidant fuel.

When HF is added to the nitric acid–dinitrogen tetroxide mixture, the following are reactions:

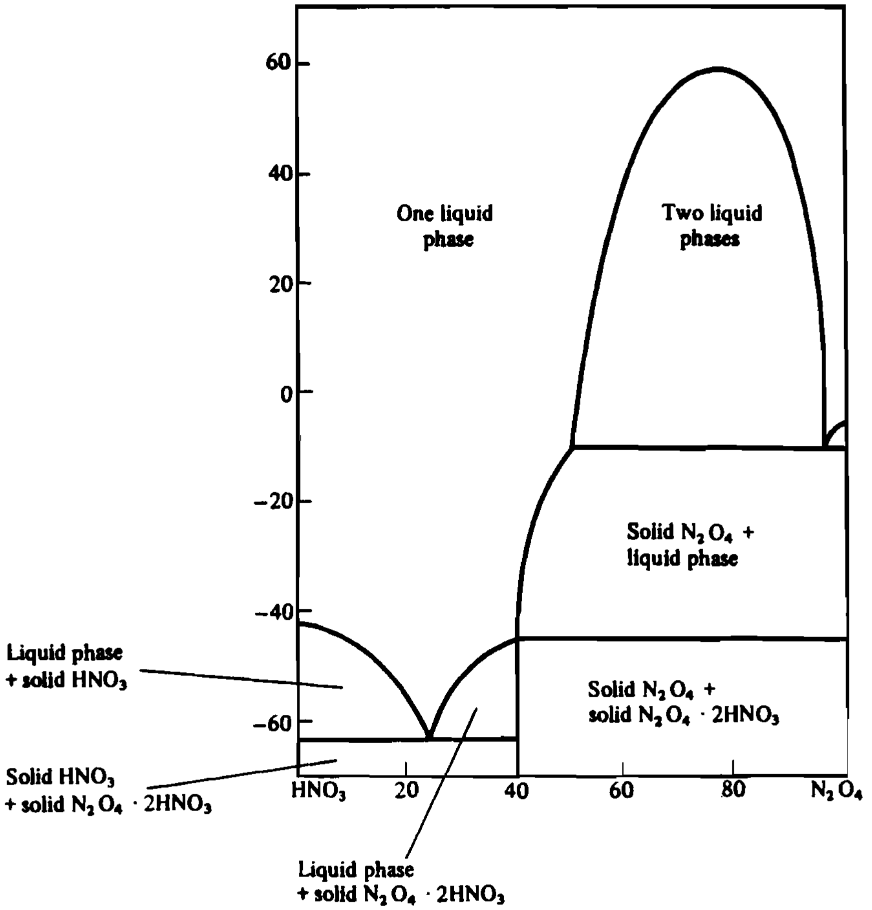


FIG. 4. Phase system $HNO_3 + N_2O_4$. (C. C. Addison [1], reproduced with permission of the American Chemical Society).

$$2\,HF + HNO_3 \longrightarrow NO_2^+ + H_3O^+ + 2F^- \tag{21a}$$

$$HF + F^- \longrightarrow HF_2^- \tag{21b}$$

$$N_2O_4 + HF \longrightarrow NOF + HNO_3 \tag{21c}$$

$$NOF + H_3O^+ \longrightarrow NO^+ + HF + H_2O \tag{21d}$$

In the presence of sulphuric acid N_2O_4 reacts as follows (Vol. I, p. 102):

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-. \tag{22}$$

This was substantiated by Raman spectroscopy and cryometry.

FRIEDEL-CRAFTS NITRATING AGENTS (Vol. I, p. 103)

The use of Friedel-Crafts catalysts in nitrating systems was originally suggested by Schaarschmidt (Vol. I, p. 103) and Topchiev (Vol. I, p. 46). Currently it is related to the concept of 'Superacids' [66, 67]. The term 'superacid' refers to acid systems which show acidity stronger than 100% sulphuric acid function H_0 [68] lower than −10.60. A superacid is usually formed by Lewis Acid and a mineral acid.

As already pointed out N_2O_4 can form complexes such as BF_3 with Friedel-Crafts catalyst.

Most mixtures of Friedel-Crafts catalysts are non-homogeneous. However, Olah [37] has found that a homogeneous system can be obtained with $TiCl_4$, BF_3, PF_5 and AsF_5 while using tetramethylene sulphone 'Sulfolan' as a solvent. Nitronium fluoride or chloride can then be formed, e.g.

$$2N_2O_4 + TiCl_4 \longrightarrow NO_2Cl + 2NOCl + TiO_2. \qquad (23)$$

Olah [33, 40] drew attention to a number of nitrating agents, such as nitronium halides (usually referred to as nitryl halides): NO_2X (X = F, Cl, Br). Nitronium chloride and fluoride were reported as nitrating agents in Vol. I, pp. 58, 107; Vol. II, p. 355 and Vol. I, p. 109 respectively. Nitronium chloride is usually prepared by reacting nitric acid with chlorosulphonic acid [69]. Nitronium bromide is unstable and was not isolated [33, 40]. According to Aynsley, Heatherington and Robinson (Vol. I, p. 109) nitronium fluoride is a more powerful nitrating agent than nitronium chloride. Infra red and Raman spectra of nitronium fluoride were examined [70].

Nitronium halides should be regarded as acyl halides and are able to take part in Friedel-Crafts acylation, which in this case is nitration, according to scheme:

$$ArH + NO_2X \longrightarrow ArNO_2 + HX. \qquad (24)$$

In the presence of aluminium halides nitronium halides react forming complex nitronium salts [33, 40]:

$$NO_2X + AlX_3 \rightleftharpoons NO_2^+ AlX_4^- \qquad (25)$$

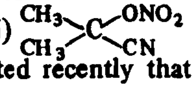
Solid Superacid Catalysts

Olah [40c] has drawn attention to the fact that the first solid acid catalyst was suggested by Kameo, Nishimura and Manabe [71]. They used polystyrenesulphonic acid with nitric acid, but the system was unstable, as the catalyst was degraded by the strong acid. Olah and associates [72] developed a nitrating agent from *n*-butyl nitrate and acetone cyanohydrine nitrate by adding a per-fluorinated resinesulphonic acid (nafion–H). It provides an exceptionally clean way of preparing nitroaromatic compounds. Nitro compounds can be isolated by a simple filtration of the catalyst, without the need of any aqueous basic washing or workup. All by-products are removed during the reaction, as they are volatile. By way of azeotropic removal of water, the nitration can be brought to a very high yield.

ALKYL NITRATES AND BORON TRIFLUORIDE

Alkyl nitrates in sulphuric acid have already been used as nitrating agents (Vol. I, p. 122). Poly(phosphoric) acid [73] and Lewis acid halides [74–76] were also used with alkyl nitrates. Olah and Lin [77] nitrated a number of aromatic compounds with methyl nitrate and BF_3 in nitromethane solution. Only mononitration took place.

Spectroscopic examination of the nitrating solutions (infra red and Raman spectroscopy) did not show the presence of a detectable concentration of NO_2^+ ion. This does not exclude the possibility of nitrating aromatics (as has already been discussed pp. 23–24). Either the system $NO_2^+ \ BF_4^-$ or a polarized complex $CH_3ONO_2 \longrightarrow BF_3$ is the nitrating agent.

Narang and M. J. Thompson [78] suggested using acetonecyanhydrine nitrate (ACN)  $(CH_3)_2C(ONO_2)CN$ and BF_3 as a nitrating agent. Olah and co-workers [124] reported recently that aromatic compounds can be nitrated with silver nitrate in acetonitrile solution in the presence of boron trifluoride at 25°C. With *p*-xylene the yield is up to 91% of mononitro compound. (See also Vol. I, p. 46).

NITRIC ACID AND MERCURY SALTS (Vol. I, p. 110)

Among different metal salts catalysing the nitration of aromatic systems, mercury salts occupy an exceptional position (perhaps tallium would also play a certain part, see p. 27).

A review on mercuric salts in nitration was given by Titov and Laptev [79]. Japanese authors: Tsutsumi and Iwata [80], Osawa and co-workers [81] have found that mercuric oxide and mercuric nitrate were catalysts of nitration with nitric acid. Komoto and co-workers [82] found that mercuric acetate catalysed nitration of toluene with nitric and acetic acid at 80°C.

Stock and T. L. Wright [83] came to the conclusion that nitration occurred in three steps:

(1) mercuration,
(2) nitrosodemercuration by the nitrosonium ion (NO^+) which exists in the nitrating mixture and is more energetic than the nitronium ion (NO_2^+) which does not produce the demercuration and only deprotonation,
(3) oxidation of the nitroso to nitro compound.

This can be depicted by a scheme established for toluene:

$$\begin{tikzcd} CH_3C_6H_5 + Hg(OAc)_2 \arrow[r] & CH_3C_6H_4Hg(OAc) + HOAc \arrow[d, "NO^+ \text{ (demercuration)}"] & (26) \\ & CH_3C_6H_4NO + Hg\,OAc^+ & (27) \end{tikzcd}$$

$$CH_3C_6H_4NO + HNO_3 \longrightarrow CH_3C_6H_4NO_2 + HNO_2. \qquad (28)$$

Inorganic Nitrate Salts and Trifluoroacetic Acid (Vol. I, p. 46)

Nitric acid salts in the presence of other acids have been previously described (Vol. I, p. 46). It was recently reported by Crivello [125] that metal nitrates in trifluoroacetic anhydride (TFAA) can nitrate aromatic compounds at room temperature in very good yields. Thus ammonium nitrate with TFAA nitrated benzene to nitrobenzene with a yield of 95%.

NITROUS ACID (Vol. I, p. 116)

Dinitrogen trioxide (nitrous anhydride) was found to have m.p. −100.7°C [84]. Its structure  $\overset{NO}{\underset{NO_2}{|}}$ was confirmed by Anderson and Mason [84] through N^{14} NMR examination.

Nitration with nitrous acid can proceed in three ways:

(1) through the addition to double bonds (Schechter [48]),
(2) through the nitrosation which is the first step of the reaction followed by the oxidation of the nitroso product,
(3) through the formation of nitric acid from the nitrogen dioxide built from nitrous acid:

$$HONO \longrightarrow N_2O_3 \longrightarrow NO{+}NO_2 \xrightarrow{[O]} 2NO_2. \qquad (29)$$

The known reaction of NO_2 with water yields equimolar proportions of HNO_3 and HNO_2. The latter can again furnish NO_2 according to (29) and finally NO_2^+ according to (5a) and (5b).

Nitrous salts in strong acids are subjected to dissociation with the formation of nitrosonium ion NO^+:

$$HONO + H_3O^+ \longrightarrow NO^+ + 2H_2O. \qquad (30)$$

The nitrosonium ion can be subjected to oxidation with the release of NO_2 and further formation of HNO_3 and HNO_2.

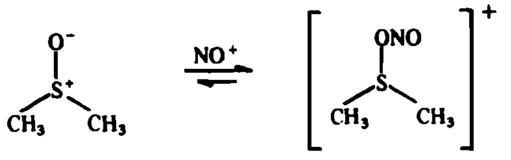
The presence of nitrosonium ion has been spectroscopically established by Singer and Vamplew [85] in aqueous (58%) perchloric acid. It showed strong bands 260 and 420 nm, and molecular HONO gave weak maxima of 340 and 390 nm. The equilibrium constant of the reaction (30) was determined by Turney and Wright [86].

It was stated by T. Urbański and Kutkiewicz [9] that 8-hydroxyquinoline could be nitrated by boiling with a dilute (*ca.* 0.3%) solution of $NaNO_2$ in 10% hydrochloric acid to yield 5,7-dinitro-8-hydroxyquinoline. If the reaction passes through the nitrosation it cannot give a dinitro product, as the nitrosation can introduce only one nitroso group. Still more convincing is the fact the 8-hydroxy-5-nitroquinoline when heated to *ca.* 90°C with *ca.* 0.4% solution of sodium nitrite in 10% hydrochloric acid produced 5,7-dinitro-8-hydroxyquinoline with 60% yield. It is known that a mononitrophenol (and thus the 8-hydroxy-5-nitroquinoline) cannot be nitrosated. Subsequently the formation of the dinitro compound is the result of nitric acid formed from NO_2 and yielding NO_2^+ according to the scheme rationalized already – reactions (5a) and (5b) (p. 24).

The view that the nitration of phenol is inconsistent with the commonly accepted prior nitrosation scheme was also expressed by Ross and co-workers [87].

A few more examples of nitration by nitrous acid should be mentioned: the nitration of *m*-fluoro-*N*-dimethylaniline [88], nitration of phenothiazine-3 [89] and phenothiazine-5-oxide [90]. They also should be rationalized by formulae (5a) and (5b).

Recently Olah and associates [91], [40c] obtained *S*- and *N*-nitrito onium ion salts (31) and (32), and found them to be electrophilic nitrating agents:



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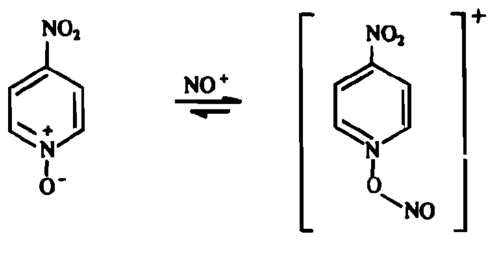


(32)

The addition of N_2O_3 to a double bond C═C was given in Vol. I, p. 96. Recently Hauff, Traillon and Perrot [92] described the addition of nitrous anhydride to α, β-unsaturated ketones of the chalcone type to yield pseudonitrosites, which were reduced with Li Al H_4 to a number of amines.

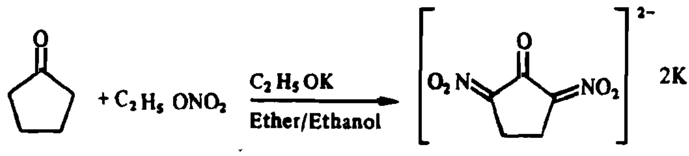
NITROSYL CHLORIDE

Nitrosyl chloride, NOCl (b.p. −5.5°C, m.p. −64.5°C) is the acid chloride of nitrous acid. As is known, it is evolved from 'aqua regia' together with chlorine and can be formed from NO and chlorine in the presence of charcoal as a catalyst at 40–50°C.

Nitrosyl chloride can be added to a double bond to yield dichlorides, dichloronitroso compounds and also chloronitro compounds of the type $Cl-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NO_2$ through the secondary reaction of oxidation [114–117].

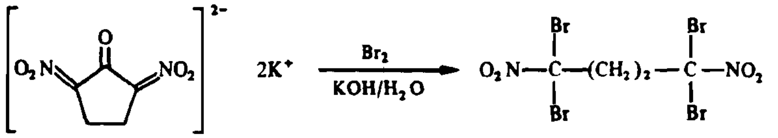
NITRATE ESTERS IN ALKALINE MEDIUM (Vol. I, p. 122)

The nitration of active methylene compounds by the action of nitrate esters under basic conditions is a general and convenient method for introducing a nitro group in α-position to the activated group. The pioneering work of Thiele [93] and Wislicenus [94] should be added to the previously (Vol. I) mentioned papers. Also the work of Wieland and associates [95] should be mentioned as producing the dipotassium salt of dinitro cyclic ketones, according to equation (33):



(33)

The authors claimed 75% yield, but Feuer and co-workers [96] obtained only 10% yield with the formation of tarry by-products. They also carried out a ring opening reaction which is already known [97]



(34)

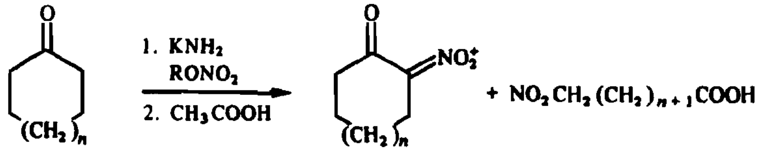
Kornblüm [98] reviewed earlier papers on the nitration of ketones and nitriles.

Feuer [99] carried out a considerable amount of work on nitration with nitrate esters and introduced a number of improvements. The basic features of his method consist in:

(a) using a stronger base than potassium ethoxide,
(b) using an aprotic solvent.

Thus he reacted on compounds with an active methylene group with a basic reagent such as sodium or potassium amide and liquid ammonia as a solvent. He summarized his earlier work in a review paper [99].

A few examples should be mentioned here. Feuer and co-workers [100] nitrated cyclopentanone, hexanone and heptanone with an excess of amylnitrate (3–3.5 eqv.) in the presence of potassium amide (3–3.5 eqv.) in liquid ammonia at −33°C obtained dinitro-dipotassium salts of the type as in equation (33) with yields of 94, 94.5 and 85% respectively. With 2 eqv. of alkyl nitrate and 1 eqv. of KNH_2 mononitration occurred with a simultaneous ring opening to ω-nitrocarboxylic ester [100, 101]:

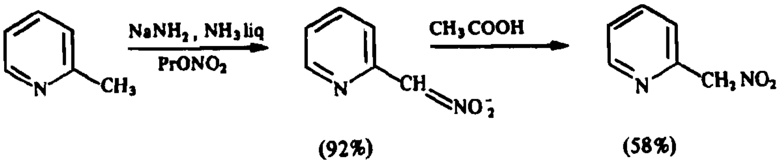


(35)

In the case of cyclooctanone the yields were: 60% mononitropotassium salt and 21% nitroester.

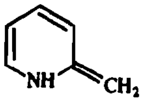
While experimenting with esters of the homologues of acetic acid $RCH_2COO.C_2H_5$ with the same nitrating agent Feuer and Monter [102] obtained not only the nitro product $R\underset{NO_2}{C}HCOOC_2H_5$ but also nitroalkanes of the type RCH_2NO_2 sometimes with a high yield (48% when $R = C_6H_5$). If $R = O_2NC_6H_5$, the nitration does not take place due to the high acidity of the nitrated compound.

An interesting application of the method of nitration of active methylene group is the nitration of methyl group in α- and γ-picoline [103], for example:

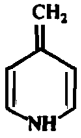


(36)

This should be rationalized (according to the author of the present book) in terms of the reactivity of tautomeric forms of α- and γ-picolins:



α



γ

Also Feuer and Friedman [104] in a similar way obtained phenylnitromethane derivatives with a yield of 40–55% by experimenting with amyl nitrate and KNH_2 in liquid ammonia at −33°C on *o*- and *p*-substituted toluene $RC_6H_4CH_3$, on condition that the substituent is an electron attracting group, for example R = CN, SO_2 C_6H_5 etc.

The same method of nitration was used to nitrate compounds with active CH groups: arylidene [105] and aldimines [106] i.e. compounds of the structure RCH = N–NH C_6H_5 and RN = CH CH_2 R respectively. Nitro compounds $R\underset{NO_2}{\underset{|}{C}} = N\ NH\ C_6H_5$ (yield 91%) $RN = \underset{NO_2}{\underset{|}{C}}\ CH_2\ R$ (yield 40–70%) respectively were obtained.

Feuer and co-workers [107] obtained nitroalkylphosphonate esters. $R\ \underset{NO_2}{\underset{|}{C}}H\ P\ (O)\ (OR)_2$ from the alkylesters R $CH_2P(O)(OR)_2$ by using a modification of his method while potassium amide in liquid ammonia proved to be unsuitable to nitrate. More energetic agents, such as butyllithium in THF or Li-diisopropylamide in THF were applied at −60°C and gave a yield of 27–41%.

Recently, Petrov and co-workers also [121, 122] published a number of papers on the nitration of active methylene groups with nitrate esters.

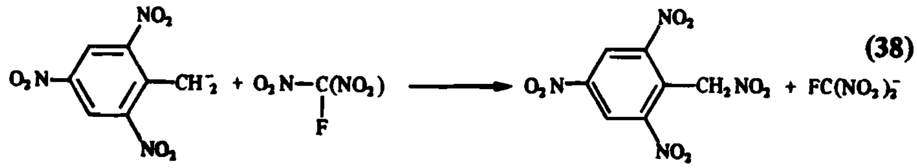
ALIPHATIC NITRO COMPOUNDS

Tetranitromethane (TNM) continued being used as a nitrating agent. An extensive review of the properties of TNM including nitration was given by Perekalin and Altukhov [118]. The property of TNM as a nitrating agent is based on the fact that one of the four nitro groups of this compound can readily be split off. The properties of TNM are described in Chapter VIII.

Penczek, Jagur-Grodzinski and Szwarc [108] described the mechanism of the nitration of 1,1-diphenylethylene with tetranitromethane. As the first step an undefined charge–transfer complex (CT) is formed which dissociates into ions reacting to yield 1,1-diphenyl-2-nitroethylene:

$$\begin{aligned}&(C\,H_5)_2\,C = CH_2 + C(NO_2)_4 \longrightarrow (CT) \longrightarrow (C\,H_5)_2\,C^+\,CH_2NO_2 + \\ &(NO_2)_3\,C^- \longrightarrow (C\,H_5)_2\,C = CH\,NO_2 + (NO_2)_3CH.\end{aligned} \qquad (37)$$

Sitzman, Kaplan and Angers [109] used fluorotrinitromethane [110] to nitrate the methyl group in 2,4,6-trinitrotoluene. The reaction was carried out in *ca.* 14% aqueous NaOH at 0–5°C followed by quenching with hydrochloric acid:

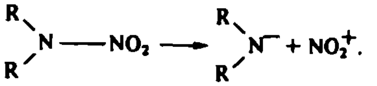


(38)

NITRAMINES (Vol. I, p. 125)

Nitroguanidine in sulphuric acid has been found to be a nitrating agent. T. Urbański and Zyłowski [111] extended this observation to other nitramines, such as nitrourea, dimethyldinitroxamide and cyclonite. They nitrated anthraquinone dissolved in sulphuric acid by adding nitramines to the solution at room temperature and keeping the solution for a few hours. With cyclonite and dimethyldinitrooxamide the yield of 1,5-dinitroanthraquinone was 34 and 77% respectively. When nitroguanidine and nitrourea were used, the solution was heated to 100–120°C and the yield of the dinitro derivative was 67%.

The reaction suggested the formation of the nitronium ion:



$$R_2N{-}NO_2 \longrightarrow R_2N^- + NO_2^+. \qquad (39)$$

Nitration with cyclonite in sulphuric acid confirms the suggestion of Šimeček (Vol. III, p. 81) that the decomposition of cyclonite in sulphuric acid yields nitronium ions.

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CHAPTER 2

NITRATION OF AROMATIC SYSTEMS

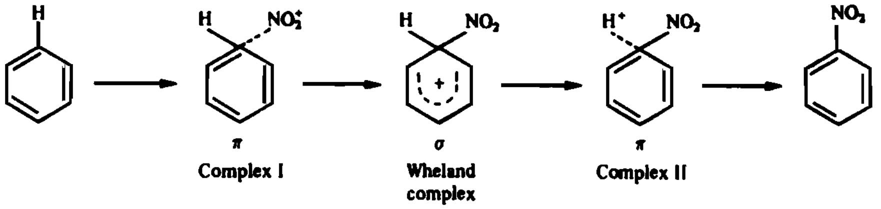
A considerable number of excellent monographs and review papers have been published on the nitration of aromatic systems and all references can be found therein [1–8]. Only main outlines will be given here.

It is now generally accepted that the nitration of aromatics proceeds stepwise. A stepwise process of substitution (known now as electrophilic substitution) was first suggested in 1901 by Lapworth [9] then by Pfeiffer and Wizinger [10], Melander (Vol. I, p. 38) but only later the idea was rationalized by a number of authors almost simultaneously due to the advent of spectroscopy and improvements of preparatory methods of new reagents.

A reference should be made to the paper by Nagakura and Tanaka [11] on the calculated reactivity of the nitronium ion NO_2^+ and aromatic hydrocarbons. They suggested the formation:

1. of an aromatic cation which is a π complex,
2. Wheland transition state with the formation of a σ complex.

This can be depicted at present by scheme (1):



(1)

A simplified energy diagram is presented in Fig. 5 based on that of Olah and associates [12, 13]. In a similar way R. D. Brown [14] considered that an electrophilic substitution begins by the formation of unstable charge–transfer complexes. R. Taylor [15] observed anomalously high and solvent dependent o/p ratios for the nitration of biphenyl and rationalized it that a π-complex between NO_2^+ and biphenyl is formed initially and rearranges to a more stable σ-complex at the *ortho* position of one of the aromatic rings of biphenyl. The final experi-

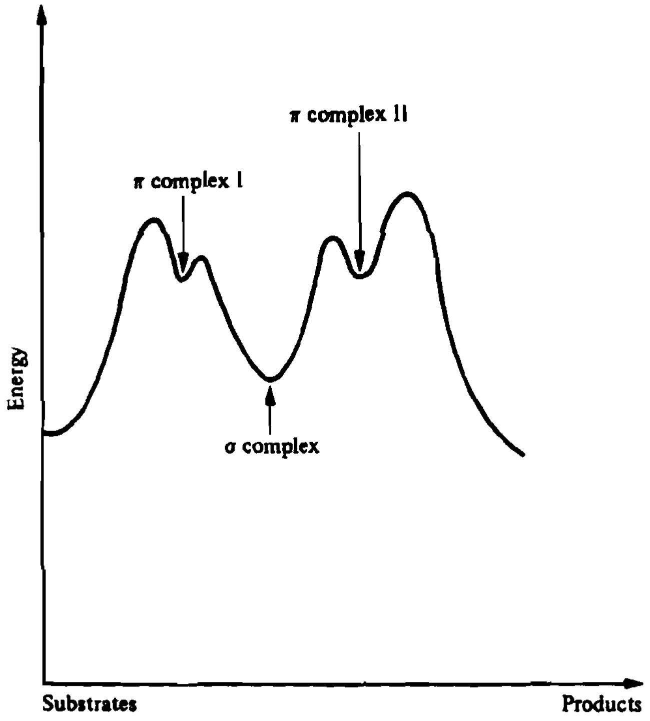
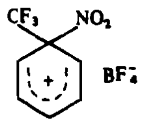


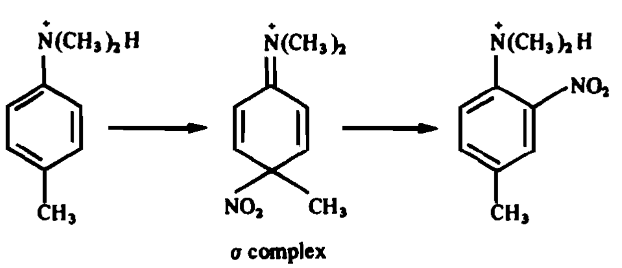
FIG. 5. Simplified energy diagram of the nitration of aromatics with nitronium ion.

mental proof for stable Wheland σ-complexes being formed as intermediates of the nitration was given by Olah and co-workers [12] when they isolated benzaltrifluoride-nitronium boron tetrafluoride



by acting on benzaltrifluoride ($C_6H_5CF_3$) with nitronium fluoride (NO_2F) and boron trifluoride at −120° to −100°C, a yellow coloured complex stable up to −50°C resulted. Olah and associates [13] pointed out that the Wheland structure is not a transition state (as σ complexes) but a relatively stable intermediate.

Recently Fujiwara and co-workers [16] found that the nitration of *N,N*-dimethyl-*p*-toluidine in 70–77% sulphuric acid proceeds by a formation of the σ complex through the *ipso*-attack (on *ipso*-nitration see p. 50) and after that the ion is rearranged to the nitro compound (2):



(2)

Ridd considered that the amino group in the nitrated compound stabilizes the σ-complex.

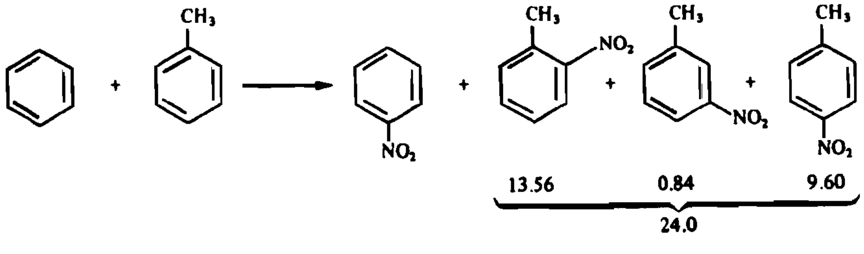
INFLUENCE OF SUBSTITUENTS ON NITRATION

Very important from both theoretical and practical points of view were experiments on the influence of substituents on the rate and the yield of nitration. For that purpose the method of competitive nitration was used. It was originally developed by Wibaut [17] to study the rate of nitration with nitric acid–acetic anhydride of toluene, chlorobenzene and bromobenzene in relation to benzene. The experiments established a higher rate of nitration of toluene and a lower rate of chloro- and bromobenzene:

$$C_6H_5CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5Br.$$

Thus it was stated that the methyl group activates the aromatic ring, whereas chloride and bromine deactivate it.

The method of competitive nitration was extensively used by Ingold and co-workers [18] and by a number of other authors. Very spectacular are the results of the relative rates of nitration of benzene and toluene obtained by Cohn and co-workers [19]. The nitration was carried out with nitric acid in nitromethane. They gave relative reactivities of each position of toluene:



(3)

Thus the relative rate of the substitution of toluene is 24.0 (benzene being postulated as 1.0).

The following is an example of the calculation of 'partial rate factors'.

The rate constant of the substitution of toluene k_T is: $k_T = 2k_o + 2k_m + k_p$, where k_o and k_m are the rate constants of one of the *o*- and *m*-positions respectively and k_p the rate constant of the *p*-position. If the rate constant of one of the positions of benzene is k_b, the total rate constant of benzene k_B is equal to $6k_b$. From this can be written:

$$\frac{k_T}{k_B} = (2k_o + 2k_m + k_p)/6k_b = 24. \qquad (4)$$

The fraction of each isomer, for example the rate at the *ortho* position relative to the total rate of the substituted benzene can be calculated:

$$\text{fraction of } o\text{-product} = 2k_o/(2k_o + 2k_m + k_p) = \frac{13.56}{24} = 0.565. \qquad (5)$$

From equations (4) and (5) the rate of nitration can be calculated of a single position in toluene to that of in benzene:

$$2k_o + 2k_m + k_p = 144\,k_b \qquad (6a)$$

and

$$2k_o + 2k_m + k_p = \frac{2k_o}{0.565}, \qquad (6b)$$

hence:

$$144\,k_b = \frac{2k_o}{0.565} \qquad (6c)$$

and

$$\frac{k_o}{k_b} = 41 \qquad (6d)$$

The value k_o/k_b is called partial rate factor in *ortho* substitutions and expressed now by symbol f_o or o_f. Similarly the partial rate factors for the other positions in toluene can be calculated:

$$\text{for } meta \text{ positions } f_m \text{ or } m_f = k_m/k_b = 2.5, \qquad (7)$$

$$\text{for } para \text{ position } f_p \text{ or } p_f = k_p/k_b = 58 \qquad (8)$$

Bird and Ingold [20] have given the following comparative figures for the nitration of toluene and chlorobenzene with nitric acid in nitromethane at 25°C – Table 11.

For partial rate factors of different hydrocarbons and under different nitration conditions see [4].

The figures of the rate constants k for the reactions of *m*- and *p*-substituted benzene derivatives have been taken for Hammett equation [21]:

TABLE 11. Isomer distribution and partial rate factors of the nitration of toluene and chlorobenzene

	Relative rates k/k_b	% Isomer distribution			Partial rate factors		
		o	*m*	*p*	o_f	m_f	p_f
Toluene	21	61.7	1.9	36.4	38.9	1.3	45.8
Chlorobenzene	0.031	29.6	0.9	69.5	0.028	0.00084	0.130

$$\log k/k_B = \rho \cdot \sigma \tag{9}$$

where:

ρ is the measure of the sensitivity of the substance to ring substitution
$\rho = 1$ in benzoic acid,
σ is characteristic to the substituent.
For nitration $\rho = -6.0$

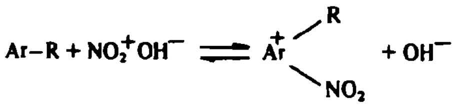
A plot of log k/k_B against σ was given by Stock [22] and reproduced here – Fig. 6.

A particular instance of nitration is *ipso*-nitration.

IPSO-NITRATION

The aromatic electrophilic substitution is usually represented by replacing a hydrogen atom with an electrophilic agent. However it was recently shown that the electrophilic attack is not restricted to aromatic carbon bonded with hydrogen. This is the case in *ipso*-nitration where the attack occurs at a substituted aromatic ring carbon. The *ipso*-reaction was placed in focus by Perrin and Skinner [23] in 1971 and two excellent review papers appeared on the subject: by Myhre [24] and by Hahn and associates [25].

A general trend of *ipso*-nitration can be depicted by scheme (10):



(10)

Ipso ion
(Nitroarenium ion)

The reaction is characterized by its reversibility. The *ipso* ion is able to further react and can be used as a valuable intermediate. By using the rate data existing in the literature [26] Myhre [24] calculated the partial rate factors of the nitration of toluene as shown in formula I. Fischer and Wright [27]: they found that the nitration of toluene at low temperature with acetic acid–acetic an-

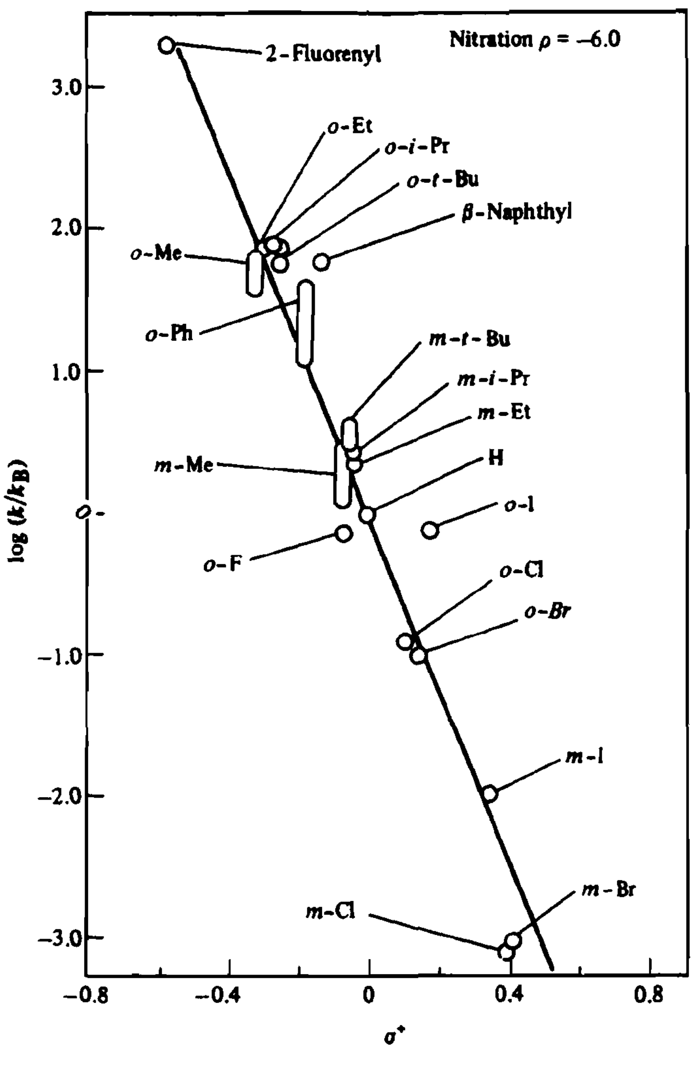
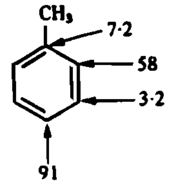


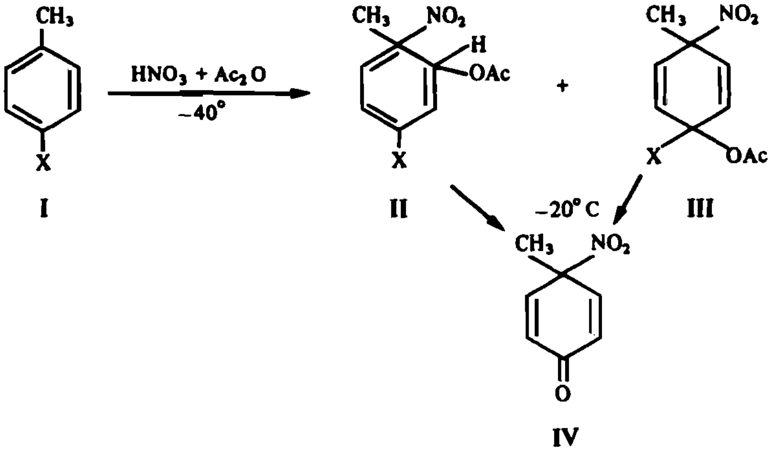
FIG. 6. Log k/k_B against σ^+ according to Stock [22].

hydride–nitric acid solution in *ipso* position is more than twice faster than in *meta* position:



Thus, surprisingly enough, position 1 is more reactive than *meta*.

While reacting–*p*–halogenotoluenes (I) with nitric acid–acetic anhydride at −40°C Fischer and co-workers [28] obtained two isomers: *ortho* II and *para* III of nitrocyclohexandienylacetates. In the instance of X = F, the overall yield was 100% and the ratio *o*/*p* = 25/75.



(11)

On warming to −20°C both isomers were converted to 4-methyl-4-nitrocycla-hexa-2,5-dienone (IV). Barnes and associates [29] reported that they prepared several 4-alkyl-4-nitrocyclohexa-2,5-dienones in good yield up to 85% by low temperature −40° to 0°C nitration of the appropriate 4-alkylphenylacetates with 90% nitric acid or acetyl nitrate in acetic anhydride.

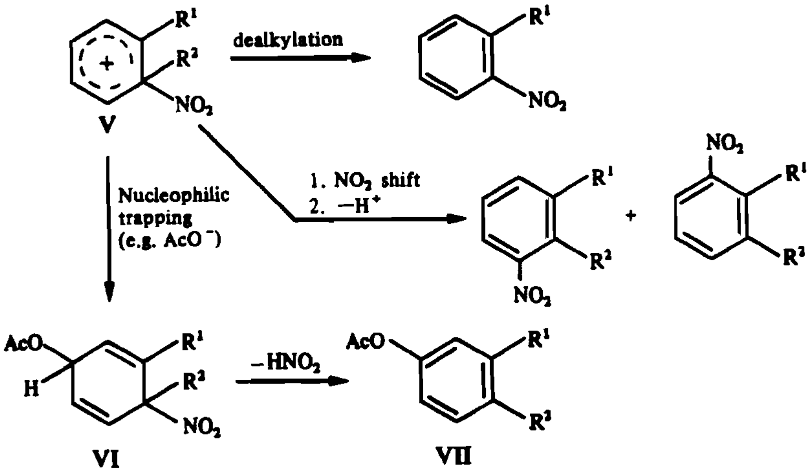
Nitration of a number of 4-substituted toluenes with a formation of *ipso*-compounds, their transformation and Hammett equation for *ipso*-nitration was also described [30].

The transformation of *ipso*-products leading to different compounds was summarized by Galley and Hahn [31]. The nitroarenium ion cyclohexadienyl cation (V) derived from *ipso* attack can undergo the reactions:

(1) dealkylation [32],

(2) nitro group migration, followed by deprotonation [33, 34],

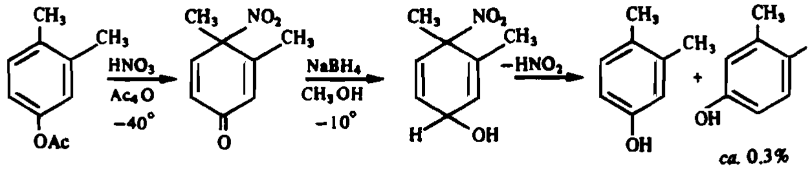
(3) nucleophilic trapping which may be followed by HNO_2 elimination [35] (12).



(12)

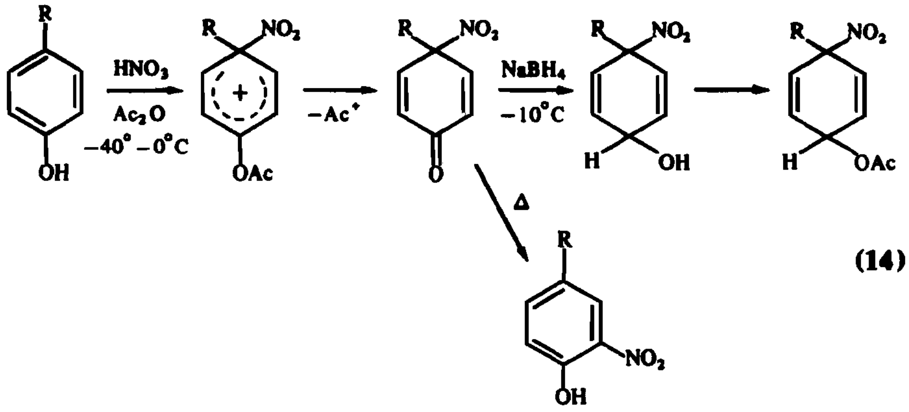
The formation of acetoxy compounds VII which was originally thought to be a result of electrophilic substitution [36] has been shown to occur as an addition–elimination reaction through the *ipso*-attack [37]. The formation of cyclohexadienyl derivatives of type VI provide a rational explanation of some non-conventional aromatic substitutions [38].

Recently Myhre and co-workers [39, 40] described the nitration of a number of 4-alkylphenol acetates to yield 4-alkyl-4-cyclahexadienones. Reduction of these dienones with sodium borohydride gave 4-alkyl-nitrocyclohexadienols which can be converted to nitrophenols. Here an interesting intramolecular migration of a hydroxyl group was recorded [39]:



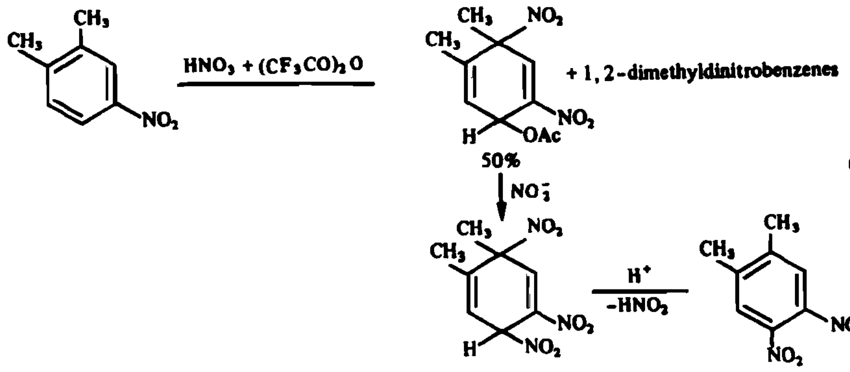
(13)

The influence of the temperature of nitration of 4-alkyl-phenol acetates was examined by the same authors [40] and simultaneously and independently by Schofield and associates [41]. The latter examined the thermal migration of the nitro group:



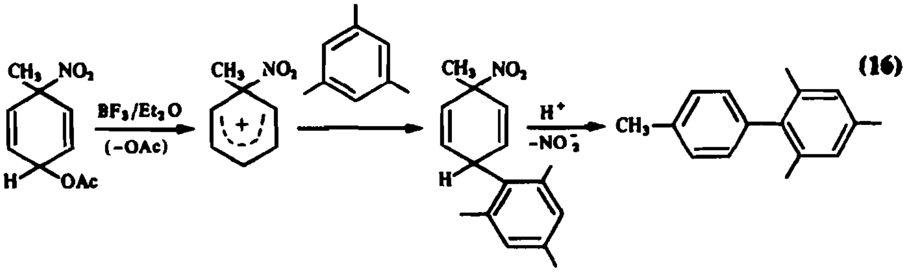
(14)

An interesting reaction of the nitration of 1,2-dimethyl-4-nitrobenzene in a mixture of nitric acid with trifluoroacetic anhydride was reported by Fischer and Iyer [42]. 4,5-Dimethyl-2,4-dinitrocyclohexa-2,5-dienyl acetate was originally formed. It reacted with nucleophiles, such as NO_2^- to yield eventually 1,2-dimethyl-4,5-dinitrobenzene:



(15)

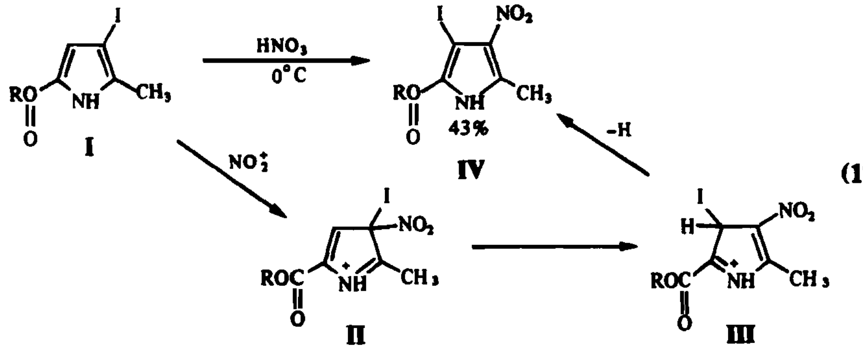
One of the possible practical applications of nitro cyclohexandienyl acetate is coupling it with some aromatics to obtain diphenyl derivatives [43]:



(16)

An interesting *ipso*-nitration of nitrofurane derivative was reported [44]. gem-Nitro compound is formed and $\overset{NO_2}{\underset{NO_2}{}}\!\!>C<$ is converted to $O = C<$.

Some recent investigations of the nitration of heterocyclic aromatic systems, such as derivatives of pyrrol should be mentioned, as they seem to support the idea of the additional mechanism of NO_2^+ in the sense of *ipso*-reaction. Thus, Sonnet [45] described the reaction:



(17)

He explains it in terms of the formation of intermediate *ipso*-addition product II which is transformed into III through the migration of iodine atom (17). The loss of the proton from III yielded eventually IV.

AROMATIC RADICAL CATION

Dynamic nuclear polarization of aromatics in the course of nitration was suggested [92] and recently Ridd and Sandal [93] gave evidence of it on the nitration of *N,N*-dimethylaniline in sulphuric acid and stated a strong polarization of 15N nuclei rationalized in terms of the formation of the radical pair $[ArH^{+\cdot}NO_2^{\cdot}]$ from the preformed radicals $ArH^{+\cdot}$ and $NO_2^{\cdot}$.

REVERSIBILITY OF AROMATIC NITRATION

It is generally accepted that the C-nitration of the aromatic system is an irreversible process. The problem has already been discussed in Vol. I, p. 41 and the conclusion was that the C-nitration group can migrate if this meets with steric hinderance, for example, the nitro group in *ortho* position to adjacent group or groups. It was also substantiated by T. Urbański and Ostrowski (Vol. I, p. 41) but the conclusion was that the mobility of the nitro group cannot be regarded as the proof of the reversibility of the C-nitration.

However, the problem was recently revived. It was recalled that Frisch, Silverman and Bogart [46] pointed out the lability of *o*-nitro group in 4-amino-3-nitroveratrole. This compound in acid condition can be transformed into 4-

amino-5-nitroveratrole when heated with acetic–phosphoric acid mixture, but the fact has not been further examined.

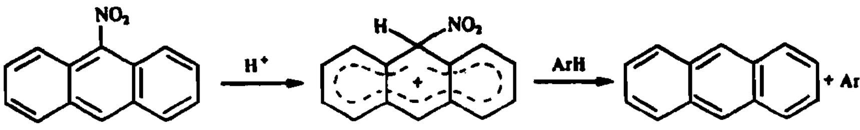
Later Gore [47] found that 9-nitroanthracene when heated with sulphuric and trichloroacetic acid to 95°C, after 15 min revealed a considerable amount of nitric acid *ca.* 80% and anthraquinone *ca.* 20%. This author suggests a scheme:

$$\mathrm{ArNO_2} \rightleftharpoons [\mathrm{ArHNO_2}]^+ \rightleftharpoons \mathrm{ArH} + \mathrm{NO_2^+} \qquad (18)$$

but when nitrobenzene was added he failed to find dinitrobenzenes.

The author comes to the conclusion that 'normal aromatic nitration' should continue to be regarded as essentially irreversible, but can be reversed in certain cases when the nitro group is in a steric hindered position.

Cerfontain and Telder [48] acquired an indication of the possible reversibility of aromatic nitration of anthracene-9-d, and finally Olah and associates [49] obtained evidence of the reversibility of the nitration of 9-nitroanthracene and pentamethylnitrobenzene when they found that these substances catalysed by superacids can yield nitrobenzene, nitrotoluene and nitromesytylene when reacted with benzene, toluene and mesitylene respectively. They suggested the mechanism as follows:



(19)

It should however be borne in mind that positions 9 and 10 in anthracene are not typically aromatic. They are manifested by a higher reactivity than positions α and β as established by MO calculation [50]. In addition 9-nitroanthracene shows a non-planar structure with the nitro group out of plane [51] as pointed out by Cerfontain and Telder [48]. This is very similar to the position of the nitro group in *o*-dinitrobenzene and all derivatives of benzene with two *ortho* nitro groups. It is well known that the nitro groups in *o*-dinitrobenzene are not planar and there is no conjugation of double bonds in this compound. The fact is also reflected in ultraviolet-absorption spectrum of *o*-dinitrobenzene which deviates from those of *m*- and *p*-dinitrobenzenes (Vol. I, p. 169, Table 20).

The degenerate rearrangement was studied by Mamatyuk and associates [52]. They showed that the rearrangement takes place through successive intermolecular 1,2-migration of the nitro group.

The conclusion should be drawn that the reversibility of nitration can occur when a nitro group in *ortho* position is displaced through steric hindrance (aromatics with two nitro groups in *ortho* position, or a nitro group is in *ortho* position to a bulky substituent, e.g. *t*-butyl group) and the nitro group is no longer planar to the aromatic ring. This is also the case for 9-nitroanthracene.

Another example of the migration of a nitro group through an *ipso*-nitro form was described by Myhre [33], Hahn and co-workers [34].

NITRATION UNDER THE INFLUENCE OF GAMMA RADIATION

(Vol. I, p. 126)

Several papers appeared after the pioneer work of Minc and co-workers (Vol. I, p. 126). Papers by Chernova and co-workers [53] and Sugimoto and co-workers [54] have shown that even dilute nitric acid (0.1–1.7 N) can nitrate aromatic compounds when subjected to gamma radiation from Co^{60}. Benzene yielded nitrobenzene and *p*-nitrophenol as the result of free radical reactions.

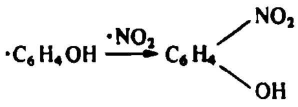
Nitric acid is decomposed by radical mechanism according to equation [55]:

$$HNO_3 \rightsquigarrow HNO_3^{*} \longrightarrow \cdot OH + \cdot NO_2 \qquad (20)$$

As a result of the formation of free radicals OH and NO_2 the following are reactions which can be rationalized through the diagrams (21) [54]:

$$C_6H_6 \longrightarrow C_6H_5^{\bullet} \xrightarrow{\cdot NO_2} C_6H_5NO_2 \qquad (21a)$$

$$C_6H_5^{\bullet} \xrightarrow{\cdot OH} [C_6H_5OH] \xrightarrow{\cdot OH} \cdot C_6H_4OH + H_2O \qquad (21b)$$



$$\cdot C_6H_4OH \xrightarrow{\cdot NO_2} C_6H_4(NO_2)(OH) \qquad (21c)$$

The yield of these reactions was found to be $G = 0.47$–0.96 G value is the number of molecules produced by the radiation energy of 100 eV. The yield is small when $G < 1$.

Falęcki, Minc and T. Urbański [56] examined the action of liquid N_2O_4 at room temperature on *n*-hexane when subjected to irradiation with Co^{60}, and obtained 1% yield of 1-nitrohexane along with a considerable amount of carboxylic acids and some nitrate esters.

Lee, Chung and Albright [57] examined the nitration of propane with nitric acid vapours at 425–430°C when propane to nitric acid ratios were 6:1 and 10:1. Gamma irradiation with 195,000 roentgens per hour from Co^{60} source of propane gas did not significantly increase the yield of the nitration, except when oxygen was added to the reactants. Also the irradiation of liquid propane prior to the reaction increased the yield by 10–15% relative percentages. The products distribution (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) was unaffected by radiation.

A number of papers were dedicated to the nitration of aromatics by gamma radiation of the aromatics present in aqueous solutions of sodium nitrate [58–61]. Broszkiewicz [59] found that sodium nitrate in the presence of oxygen yielded *o*-nitrophenol from benzene (yield $G = 41$). Chernova and Orekhova [58] obtained nitrobenzene (yield $G = 0.2$) when irradiation was carried out in an atmosphere of nitrogen.

Nowak [62] examined the influence of radiation on the system dodecane – 30% TBP tributyl phosphate – nitric acid used as extractants of burned up nuclear fuel and found that nitro compounds were formed even at low concentrations of nitric acid. Nitroso and carbonyl compounds were also formed.

INDIRECT METHODS OF INTRODUCING A NITRO GROUP

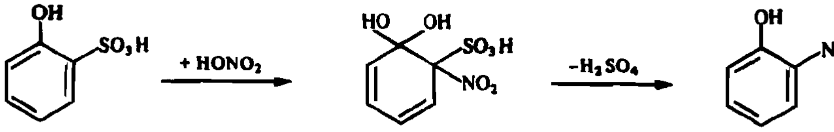
Substitution of Sulphonic Group (Vol. I, p. 126)

In addition to the work of Marqueyrol, Carré and Loriette (Vol. I, p. 500), and Pascal (Vol. I, p. 501), two more papers should be mentioned: by King [63], Olsen and Goldstein [64]. King pointed out the importance of the presence of phenol-2,4-disulphonic acid and *p*-phenolsulphonic acid in the sulphonated phenol, whereas Olsen and Goldstein suggested that the nitration of sulphonated phenol involves, in the first stage, the introduction of nitro groups into the aromatic ring. In the light of more recent investigations by T. Urbański and Leśniak [65a], it was found that two processes run simultaneously:

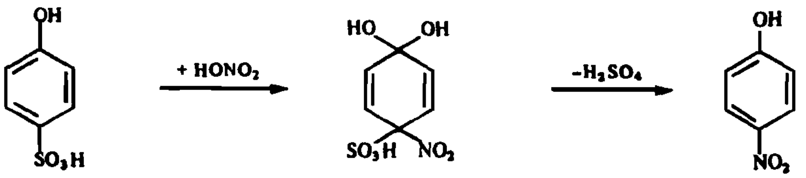
(1) introduction of a nitro group into phenol–sulphonic acid,
(2) substitution of the sulphonic group.

This was established by the chromatopolarographic method of Kemula [65b].

Also it was rationalized [65] that by reacting nitric acid on *o*- and *p*-phenolsulphonic acid coloured quinoid intermediate additions products are transformed into nitrophenol:



(22a)



(22b)

Substitution of Diazo Group

The well known reaction of Sandmeyer [66a] was suggested by Waters [66b] in terms of free radical intermediates generated by electron transfer. Russell [66c] rationalized the reaction with a stable nitroaromatic anion where copper metal serves as the electron donor and cuprous ion as the electron acceptor (23):

$$\mathrm{ArN_2^+ + Cu \longrightarrow Cu^+ + [ArN_2^{\bullet}] \longrightarrow N_2 + Ar^{\bullet}}$$

$$\mathrm{Ar^{\bullet} + NO_2^- \longrightarrow ArNO_2^{\bullet-}} \qquad (23)$$

$$\mathrm{ArNO_2^{\bullet-} + Cu^+ \longrightarrow ArNO_2 + Cu.}$$

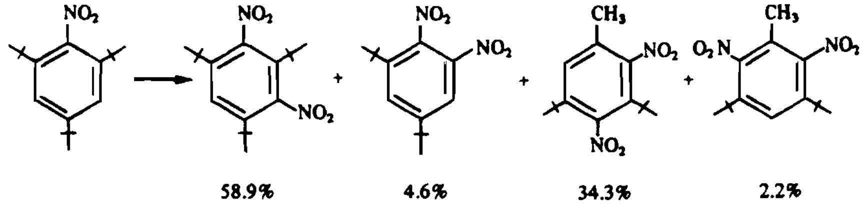
Substitution of Halogen (Vol. I, p. 127)

The reaction of Kornblum (Vol. I, p. 127) became a much more convenient method of making longer chain nitroalkanes.

In halogen derivatives of benzene, halogen can be replaced by the nitro group under the action of nitric acid. The first paper on the subject by Zinke [67] should be mentioned.

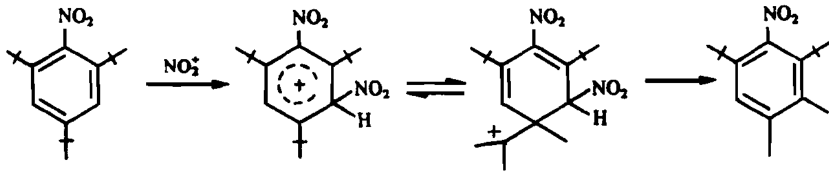
Substitution of t-Butyl Group

The nitration of 2,4,6-tri-*t*-butylnitro benzene leads to several unexpected products as shown by Myhre and Beng [68] (24):



(24)

In addition to the replacement of *t*-butyl by the nitro group a transformation of *t*-butyl into the methyl group was established. This is rationalized in terms of the reactions:



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INTRODUCING THE NITRO GROUP BY OXIDATION (Vol. I, p. 131)

Oxidation of Primary Amino Group

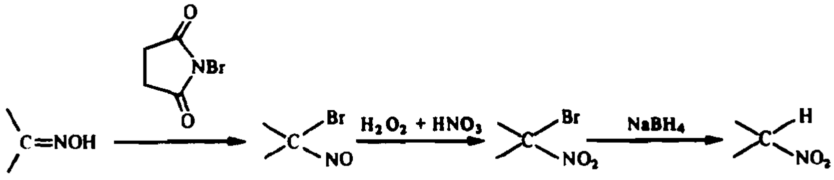
Oxidation of primary amino group in aromatic compounds by peroxytrifluoro acetic acid has been reported by Clarke and Steele [69]. The yield was 90%.

A much spectacular achievement was recently obtained by Nielsen and co-workers [70]. By oxidizing the primary amino group attached to a benzene ring bearing a number of nitro groups, polynitrobenzenes were obtained. Thus, by oxidizing 2,3,4,6-tetranitroaniline and pontanitroaniline they obtained penta-nitro- and hexanitrobenzene respectively. They used peroxy disulphuric acid (98% hydrogen peroxide in sulphuric acid or oleum at 25°C) as an oxidizing agent.

Further use of this oxidant to produce a number of polynitro aromatics was reported by Nielsen and co-workers [71] in their remarkable paper. The authors also reviewed work on the other oxidants used to pass from HN_2 to NO_2: Caro acid, peracetic, permaleic, *m*-chloroperbenzoic and perbenzoic acids. They pointed out that the power of the oxidant is proportional to the acid strength of deoxy peracid. Peracetic and *m*-chloroperbenzoic acids are suitable for the oxidation of aliphatic primary amines, whereas peracetic, peroxytrifluoroacetic and peroxymaleic acids are best for the oxidation of ring substituted anilines. Potassium persulphate in sulphuric acid was also used successfully [71].

Oxidation of Oximes

Iffland and co-workers [72] described an original method of forming nitro derivatives of alicyclic compounds by the oxidation of oximes:



(26)

The first step was the bromination of the oxime with bromocuccinimide to yield a bromonitroso compound on which the oxidation of hydrogen peroxide with nitric acid was transformed into bromonitro compound. The latter by acting with sodium borohydride furnished a secondary nitro compound with a yield of 33–80%. The method was particularly suitable for the formation of nitro derivatives of nitro cycloalkanes. The method is unsuitable for aromatic ketoximes and aldoximes. However, Barnes and Patterson [73] extended the method to aldoximes by using ozone as an oxidizing agent on gem-chloronitroso compounds. The removal of chlorine was accomplished by palladium. Piotrowska, Sas and Winiarski [74] used the Adams catalyst for the removal of chlorine.

Emmons and Pagano [75] succeeded in oxidizing oximes of alicyclic ketones with trifluoro peracetic acid to yield nitrocyclopentan and nitrocyclohexane with the yield of 60–62%. Oximes of steroids were oxidized with nitric acid–hydrogen peroxide to yield gem-dinitro derivative which under hydrogenation on platinum gave nitrosteroids with the nitro group in positions 3, 4, 6, 7 and 17 [76].

DIFFUSION CONTROL IN NITRATION

The importance of diffusion in chemical kinetics was pointed out by Eyring in 1936 [77], and subjected to a wide description by Glasstone, Laidler and Eyring [78]. The applicability of the principles of the diffusion control in various reactions and the nitration among them was recently reviewed by Ridd [79].

For reaction in solution the analysis of diffusion control is usually based on the concept of a molecular encounter. When two solute molecules come together in a solution they are effectively held within a cage of solvent molecules and make a number of collisions with each other within this cage. Such a set of repeated collisions is termed an encounter. The lifetime of each encounter is very short, 10^{-10} to 10^{-8} sec.

While considering the influence of the encounter rate on chemical reactivity a microscopic and macroscopic diffusion control should be mentioned. In microscopic diffusion control, the reactants exist together in a homogeneous solution and the reaction occurs on every encounter.

The term macroscopic diffusion control describes processes in which the rate of the reaction is determined by the rate of mixing of the reactant solutions.

According to Ridd [79] the clearest evidence for microscopic diffusion control in nitration comes from the kinetic studies of Coombes, Moodie and Schofield [80] with low concentration of nitric acid in 68.3% sulphuric acid as a solvent. In this medium the concentration of nitronium ions is proportional to the concentration of molecular nitric acid according to equation (27):

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O. \tag{27}$$

Since the concentration of nitronium ion is very small the rate of the nitration is determined by equation (28):

$$\text{Rate} = k\,[\text{ArH}]\,[\text{HNO}_3]. \tag{28}$$

Relative rate coefficients from (28) are listed in Table 12. The most interesting feature of the results according to Ridd [79] is the limiting reaction rate of

TABLE 12. Relative rates of nitration at 25°C by nitric acid in various media

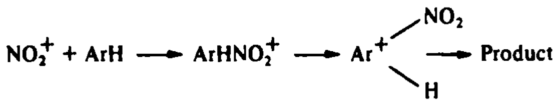
Substrate	Sulphuric acid 68.3%	Perchloric acid 61.03%	Sulfolan 7.5% aq	Acetic acid 8–19% aq
1.	2.	3.	4.	5.
Benzene	1*	1*	1*	1*
Toluene	17	19	20	23
o-Xylene	38		61	
m-Xylene	38		100	136
p-Xylene	38	85	114	
Mesitylene	36	78	350	
Anisole	13†		175	
Phenol	24	31	700	
m-Cresol		59		
Biphenyl	16		15.5	
Naphthalene	28	27	33	*ca.* 66
I-Naphthol		85		
Thiophene		52	*ca.* 150	

* Postulated.

† According to Barnett *et al.* [81].

the compounds being about forty times the reactivity of benzene. This limit is quite inconsistent with the predictions of the additivity principle. From the additivity principle and the partial rate factors for the nitration of toluene the reactivities of *m*-xylene and mesitylene would be expected to exceed that of benzene by factors of 400 and 16,000 respectively [80].

Thus the limiting reaction rate does not arise from the rate of formation of the electrophile NO_2^+ and from a general breakdown in the additivity principle. The authors [80] suggest that the limit arises from the rate-determining formation of an encounter pair ArH NO_2^+ between the nitronium ion and the aromatic substrate according to scheme (29):



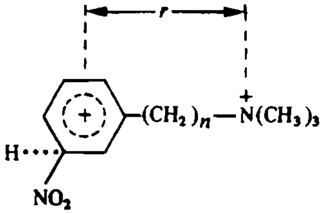
$$NO_2^+ + ArH \longrightarrow ArHNO_2^+ \longrightarrow Ar^+\begin{matrix}NO_2\\ H\end{matrix} \longrightarrow \text{Product} \qquad (29)$$

A number of Swiss authors described their experiments on mass diffusion and the influence of mixing on nitration: Ott and Rys [82], Pfister, Rys and Zollinger [83].

Schofield and co-workers [94] determined the half life of the nitronium ion on nitration of benzene in the presence of phosphoric acid of the concentration 90.3 to 97.9%. The values were found to be 2 to 33 (increasing with the concentration of H_3PO_4). On the basis of these data they concluded that nitration with NO_2^+ is diffusion controlled at H_3PO_4 over 95%.

INFLUENCE OF A POSITIVELY CHARGED SUBSTITUENT

Ridd [6] examined the influence of positively charged substituent on the yield of *para* and *meta* product of nitration. He found that $-\overset{+}{N}H_3$ deactivated the position *meta* much more strongly than *para*. Modro and Ridd [95] rationalized the influence of a positively charged substituent on the reacttion of nitration of compounds taking into consideration the distance r between two positive charges in the Wheland intermediate:



IV

Thus when $n = 0$ the partial rate factor f_m was 0.9×10^{-7}. When $n = 2$ and 3 the values for f_m were 0.13 and 0.47 and the yield of *meta* derivative was 19 and 5% respectively.

SIDE REACTIONS (Vol. I, pp. 75, 437)

Nitrating medium, that is, nitric acid or mixtures of nitric acid with sulphuric acid or other agents promoting the formation of nitroxonium cation, is obviously a strongly oxidizing medium, hence a number of side reactions – mainly oxidation reactions – take place during nitration. This was described in Vol. I (pp. 75, 437) and more recently reviewed in a number of excellent papers [84–86].

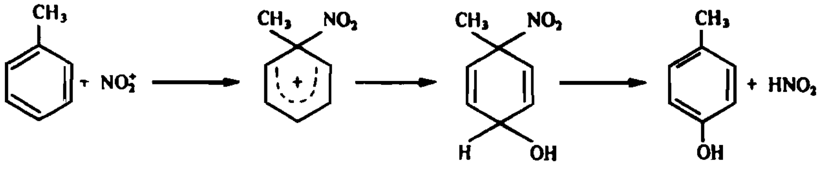
It is generally accepted that nitric dioxide and nitrous acid are catalysts of oxidation reactions. Thus Ross and Kirshen [84] came to the conclusion that the NO_2 evolved in the equilibrium

$$2\,HNO_3 \longrightarrow \tfrac{1}{2}\,O_2 + H_2O + 2\,NO_2, \qquad (30)$$

is the active oxidizer. This was based on their study of the action of nitric acid/sulphuric acid on dinitrotoluenes. The oxygen evolved in (30) is the oxidizing agent.

A striking fact was reported by Longstaff and Singer [87]. They found that formic acid cannot be oxidized by pure nitric acid alone or in mixtures with other mineral acids at 25°C, but oxidation took place in the presence of nitrous acid or NO^+ ion. Halahan and co-workers [88] studied the oxidation of several dinitrotoluenes in the course of their nitration and found that the relative rates of oxidation were in direct inverse relationship to their rates of nitration.

Hanson and co-workers [85] pointed out that nitro compounds with phenolic function are the main by-products of nitration of aromatic hydrocarbons. A number of papers by Dodak and co-workers [89] were dedicated to the formation of phenols in the course of nitration of hydrocarbons. However, the idea of phenols being formed through the action of NO^+ ion does not seem to be feasible on the experimental grounds that the addition of urea to the nitrating mixture does not prevent the formation of phenols and the addition of sodium nitrite does not foster the formation of nitrophenols [85]. Hanson rationalized the mechanism of formation of nitrophenols by an *ipso*-attack of NO_2^+ on hydrocarbon (31):



(31)

Phenols on nitration can yield derivatives of *p*-benzoquinone, for example [90].

Gaseous products which accompany the nitration are CO and CO_2. Toluene on nitration to trinitro derivative forms tetranitromethane (the mechanism of its formation is given in the chapter dedicated to the production of trinitrotoluene). Chlorobenzene and other chlorinated aromatic hydrocarbons yield chloropicrin.

In papers dedicated to side reactions to nitration, no attention has been paid to the formation of ammonia in the course of the reaction. It is formed from hydrogen cyanide produced by drastic decomposition of nitro compounds. This was discussed in detail in Vol. I, pp. 76–77. The mechanism of the formation of HCN from C-nitro compounds also explains the fact that these nitro compounds yield ammonia in Kjeldahl analysis, where the substance is subjected to the action of oleum at high temperature.

A very important oxidation by-product of the nitration of toluene to trinitrotoluene is so called 'white compounds'. It was found in the course of continuous methods of nitration of toluene.

Its structure is dicarboxy-tetranitroazoxybenzene as shown by Joshi and Patwardhan [91]. The formation and proof of the structure will be given in the chapter on formation of trinitrotoluene.

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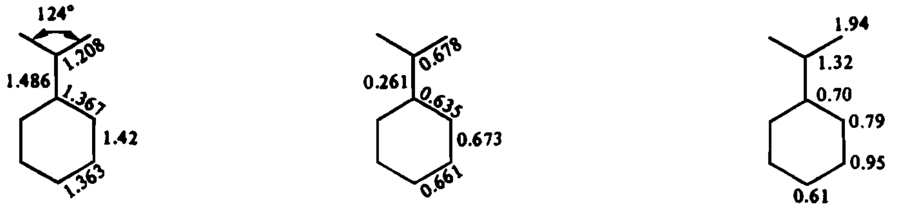
CHAPTER 3

STRUCTURES AND PHYSICO-CHEMICAL PROPERTIES OF NITRO COMPOUNDS

(Vol. I, p. 165)

A few excellent reviews appeared recently on the structure of the nitro group and the spectroscopy of nitro compounds [1–5] including mass spectroscopy of nitro derivatives of arenes and heterocycles reviewed by Khmelnitskii and Terentyev [145] and particularly on the C—NO_2 bond [3]. Thus only some problems related to the nitro group will be given here.

The geometry of the nitro group and electron density is depicted in the diagrammatic presentation of the molecule of nitrobenzene [3]:



Bond lengths **Bond orders** **π-Electron density distribution**

Nitrobenzene

FIG. 7. Geometry and electron density in nitrobenzene (according to Wagnière [3]).

Four p_x electrons of oxygen and nitrogen are present in the nitro group. They are used for π bonding and belong to the three p_x atomic orbitals *AO* – one from nitrogen and one from each oxygen atom. These *AO* combine three nitro molecular orbitals *MO* one of which is bonding π_1 Fig. 8a, one antibonding π_3^* Fig. 8b and one non-bonding π_2 Fig. 8c.

The diagram also includes the lone-pair orbitals: two and *sp* hybrid orbitals of the two oxygen atoms slightly split in the NO_2 group because of the interaction between the two atoms.

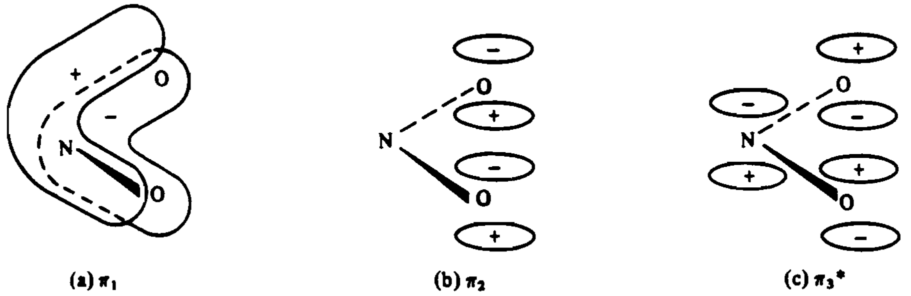


FIG. 8. The three atomic orbitals of the nitro group: (a) bonding, (b) anti-bonding, (c) non bonding (according to Jaffe and Orchin [1]).

ELECTRONIC SPECTRA OF THE NITRO GROUP

The nitro group is a chromophore. In the visible and ultraviolet absorption spectra bands π (bonding) $\rightarrow \pi^*$ (anti-bonding) and n (non-bonding) $\rightarrow \pi^*$ occur most frequently in conjugated molecules including aromatics [1–7].

The energy level – diagram is given in Fig. 9.

The classical example of the spectrum of a nitro compound is that of nitromethane. It consists of two broad bands; a high intensity band at λ_{max} = 210 nm ($\log \epsilon = 4.2$) and a weak band at λ_{max} = 270 nm ($\log \epsilon = 1.3$) which probably arise from $\pi_2 \rightarrow \pi_3$ and $n_a \rightarrow \pi_3^*$ transitions respectively. Theoretically a third band $n \rightarrow \pi^*$ from the transition $n_S \rightarrow \pi_3^*$ is also present at a very low wave-length in the 'vacuum' ultraviolet and is of low intensity. Ultraviolet-spectra of nitroalkanes including polynitro compounds were described in detail by Slovetskii [6] and reviewed by Novikov *et al.* in their monograph [7].

Attention should be drawn to the fact that polynitro aliphatic compounds such as 1,1-dinitroalkanes and trinitromethane exhibit a cloud in aqueous solutions. This is attributed to the presence of the anion [8].

Nitroalkenes (nitroolefins) are marked by the conjugation of double bonds with those of the nitro group. They show a high intensity absorption band due to $\pi \rightarrow \pi^*$ transition within the range 220–250 nm. The $n \rightarrow \pi^*$ band is strongly overlapped there by the intense red shifted $\pi \rightarrow \pi^*$ absorption band. The spectra of nitroalkenes are reviewed by Perekalin and Sopova [9] and Novikov and associates [7].

The following are data in ethanol [4] which illustrate the effect of lengthening the conjugated system in aliphatic unsaturated compounds Table (13). Kochany and Piotrowska [10] examined the ultraviolet-spectra of a number of nitroalkenes. Their $\pi \rightarrow \pi^*$ were observed between 360 and 420 nm. The ultraviolet absorption spectra of nitroethylene, nitropropenes and nitro methane have been taken and interpreted with the Pariser-Parr-Pople self-consistent field – *MO* calculation. The absorption bands $\pi \rightarrow \pi^*$ are in good agreement with calculated values [11].

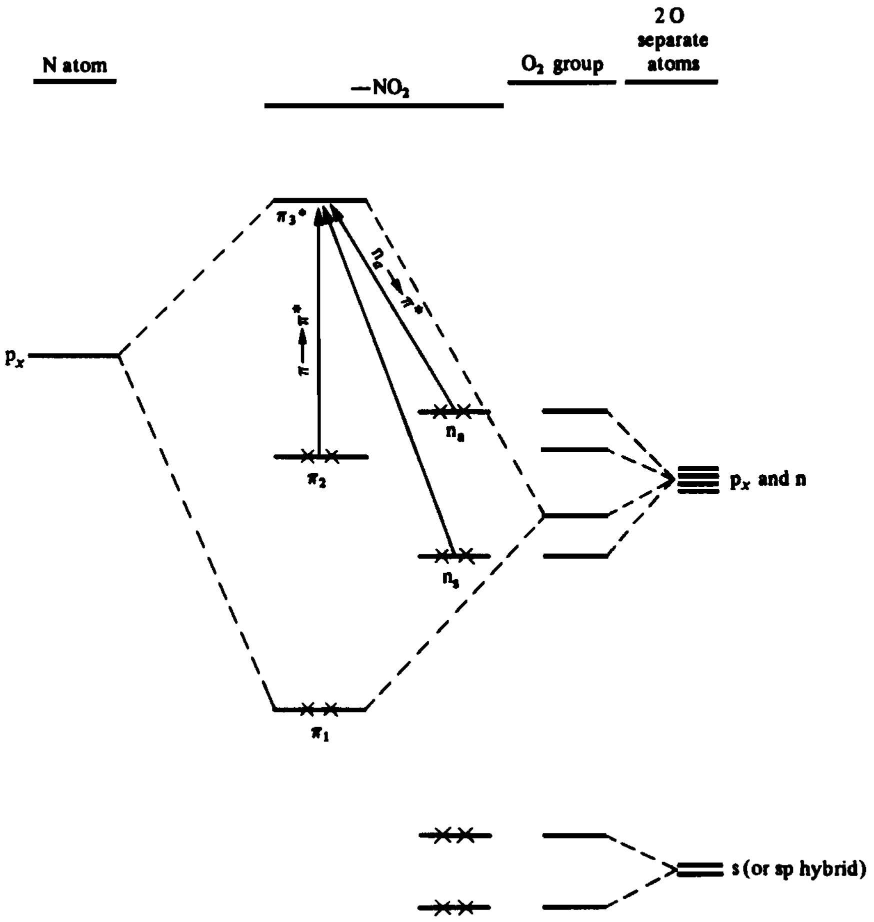


FIG. 9. Energy levels of the nitro group (according to Jaffe and Orchin [1]).

TABLE 13. Effect of lengthening the conjugated system in aliphatic unsaturated compounds

Compound	max nm	max	Transition
Nitromethane	210	5000	$\pi \rightarrow \pi^*$
	270	20	$n \rightarrow \pi^*$
1-Nitropropene-1	229	9400	$\pi \rightarrow \pi^*$
	235	9800	
	ca. 300–330 (shoulder)		$n \rightarrow \pi^*$
1-Nitro-1,3-pentadiene	227	9500	$\pi \rightarrow \pi^*$
	309	16500	

The nitro group in aromatic systems causes strong bathochromic shifts of all the aromatic absorption bands when the nitro group is attached immediately to the aromatic ring. This is the consequence of the fact that the nitro group is strongly electron attracting. Figure 10 shows the spectra of toluene, phenylnitromethane and nitrobenzene.

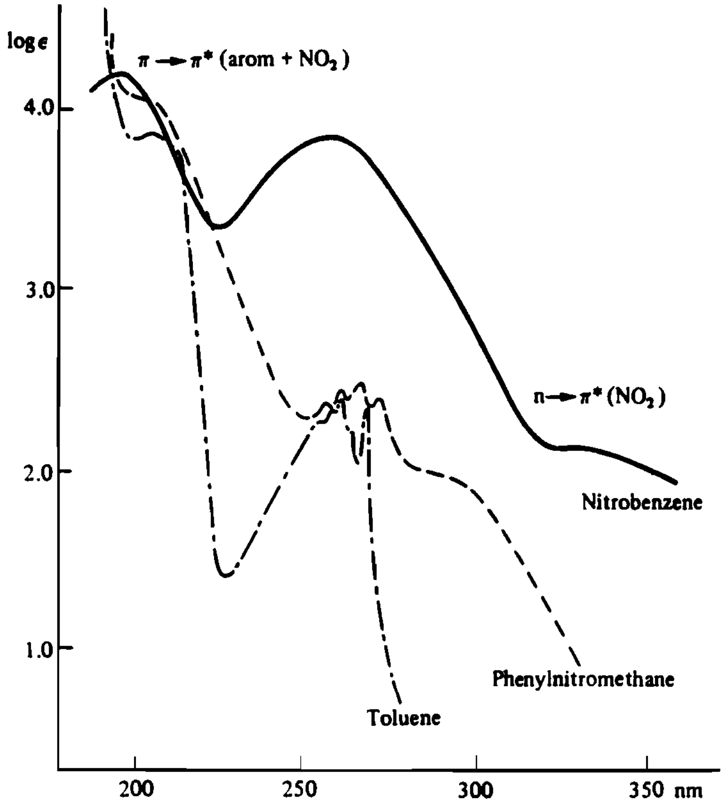


FIG. 10. Electronic spectra of phenylnitromethane and nitrobenzene (according to Buchowski and Skulski [41]).

When the nitro group is not directly attached to an aromatic ring as in phenylnitromethane then the $\pi \rightarrow \pi^*$ bands are only weakly affected by the nitro group and they do not differ appreciably from that of toluene [2].

The band around 260 nm has been assigned by Nagakura and co-workers [12] as being produced in *ca.* 6% by the internal charge–transfer structure.

Extensive study of numerous *para*-substituted β-nitrovinyl- and β-nitropropenylbenzenes were carried out by Skulski and co-workers [13]. Both groups are weaker electron attracting than the nitro group.

The nitro group attached to an aromatic ring takes part, as a rule, in the conjugation of double bonds of the aromatic ring. However, a considerable deviation of λ_{max} of aromatic $\pi \rightarrow \pi^*$ band of *o*-dinitrobenzene as compared with *m*- and *p*-isomers (Table 20, Vol. I, p. 169) is due to the fact that nitro groups in *o*-dinitrobenzene are being twisted off the aromatic plane. This was substantiated by X-ray analysis. Subsequently there is no conjugation of double bonds of that nitro group with the double bonds of the aromatic ring.

Conduit [14] examined ultraviolet and infra-red spectra of several mono-, di- and trinitro derivatives of benzene and toluene and interpreted them in terms of polar and steric effects.

The striking examples are *o*-dinitrobenzene, 2,3-dinitrotoluene and 3,4-dinitrotoluene which show $\pi \rightarrow \pi^*$ peaks at < 210, and 219 nm respectively, whereas all other dinitro compounds examined show peaks between 242 and 283.5 nm. Derivatives of toluene show peaks at a higher wave length probably due to the hyperconjugation of the methyl group.

The trinitro derivatives of benzene and toluene give bands within 227–258 nm. Here, according to Conduit, can exist a mutual reduction of conjugation by the nitro groups. The mean frequencies for the mono-, di- and trinitro compounds are 36,670, 41,760 and 41,970 cm^{-1} respectively i.e. λ_{max} 273, 239 and 238 nm respectively.

The twisting from the plane in some high nitrated derivatives of aniline was examined by Kamlet and co-workers [15].

The figures are given in Table 14.

TABLE 14. Ultraviolet spectra of ring substituted picramides in dioxane

Compound	λ_{max}	nm
Picramide	318	408
2,3,4,6-Tetranitroaniline	320	402
2,3,4,5,6-Pentanitroaniline	316	400
3,3-Diamino- 2,2′,4,4′,6,6′,-hexanitrodiphenyl	326	394

They calculated the angle of twist θ for the nitro groups in 2,3,4,6-tetranitroaniline according to Braude equation [16] and compared it with the X-ray crystallographic data of Dickinson, Stewart and Holden [17] (Table 15).

TABLE 15. Angles of twist θ in 2,3,4,6-tetranitroaniline

Substituent	Angle θ Calculated	Angle θ Observed
$2-NO_2$	21°	19°
$3-NO_2$		64°
$4-NO_2$	42°	45°
$6-NO_2$	0°	3°

An example of the steric influence on the ultraviolet-spectrum of the nitro group in non-aromatic systems was given by T. Urbański, Piotrowska and Kędzierski [18]. Absorption bands of the nitro group ($\pi \rightarrow \pi^*$) in 5-nitro-1,3-dioxane were found to be 279 and 283 nm respectively. This was confirmed by Eliel [19].

A few more papers should be mentioned as regards electronic spectra of aromatic nitro compounds: nitrobenzene, dinitrobenzene and trinitrobenzene [20] and the work of Barth [21] who subjected mono-, di- and tri-nitrobenzenes and toluenes to detailed spectrophotometric ultraviolet-visible studies and developed a quantitative analysis of TNT in the presence of cyclonite, octogene and waxes.

Theoretical calculation of $\sigma + \pi$ electronic structure of nitrobenzenes and nitrotoluenes were carried out by LCAO method and gave a good agreement with electronic spectra and dipole moments [22]. Later the CNDO and *ab initio* calculation for nitro-, dinitro- and trinitrobenzenes gave a very good agreement with spectral features and dipole moments [23].

SOLVENT EFFECT

A very prominent effect is of solvent upon the $\pi \rightarrow \pi^*$ aromatic band in aromatic nitro compounds. When given spectra of organic compounds, thought should be given to the solvent used. This is particularly important in the ultraviolet region. Schubert and Robins [24] give some figures for nitrobenzene in some common solvents – Table 16.

TABLE 16. Ultraviolet absorption of $\pi \rightarrow \pi^{\times}$ aromatic bands of nitrobenzene

Solvent	λ_{max}, nm
Water	267.5
95% Ethanol	259.7
t-Butanol	257.7
t-Butyl chloride	257.1
iso-Pentane	250.1
Acetonitryl	261.0
Nitrobenzene in gas phase	239.0

Solvatochromic shifts in the ultraviolet-visible absorption spectra of *p*-nitrophenol and *p*-nitroaniline have been taken as measures of relative solvent affinities [25].

It should be borne in mind that the acidity and basicity of the examined compounds and the use of some solvents can influence the ionic dissociation (the equilibrium acid–base) in a more appreciable way and produce the change of λ_{max} and the intensity, in electronic spectra.

INFRA-RED AND RAMAN SPECTROSCOPY

Numerous published papers have dealt with infra-red and Raman spectroscopy of nitro compounds. A general description is given in the monograph by Bellamy [26] and more recent reviews by Rao [27] and for non-aromatic nitro compounds by Novikov and co-authors [7].

The following are fundamental frequencies for nitromethane, the simplest nitro compound: Table 17.

TABLE 17. Fundamental frequencies for infra-red and Raman spectra of nitromethane according to Popov and Shlyapochnikov [28]

Vibrational class	Vibrational motion	Frequencies cm^{-1}	Intensity
Asymmetric	NO_2 asym stretching	$\nu_{as} = 1582$	vs
Symmetric	NO_2 sym stretching	$\nu_s = 1384$	s
	C–N stretching	$\nu = 921$	w
Deformation	ONO	$\delta = 647$	m
Non-planar	NO_2 bending	$\rho = 599$	w
Deformation	C–NO non-planar	$\delta = 476$	vw

Popov and Slyapochnikov [28] were able to calculate force constants in the molecule of nitromethane and Novikov [7] extended the calculation to a number of nitro compounds.

Slovetskii and co-workers according to [7] examined the frequencies of principal NO_2 bands for primary, secondary and tertiary nitro groups (Table 18).

TABLE 18. Mean ν values of frequencies of mononitro alkanes

Compounds	ν_{as}	ν_s
RCH_2NO_2	1554 ±6	1382 ±6
$RR'CHNO_2$	1550.5 ±2.5	1360 ±3.5
$RR'R''CNO_2$	1538.5 ±4.5	1348.5 ±4.5

Bellamy [26] collected information on the range of two main bands of aliphatic and aromatic nitro compounds:

asymmetric 1650–1500 cm^{-1},
symmetric 1350–1250 cm^{-1}.

Higher nitrated alkanes, for example, di- and trinitromethane show a splitting of the bands of symmetric vibrations. Thus Levin and Legin according to [7] reported bands for dinitromethane:

asymmetric: 1580 cm^{-1},
symmetric: 1386 and 1350 cm^{-1}.

The frequency of deformation vibrations $\delta(ONO)$ cm^{-1} is strongly influenced by the number of nitro groups [7]:

CH_3NO_2	$\delta =$ *ca.* 650 cm^{-1}
$CH_2\ NO_{2\ 2}$	*ca.* 402 cm^{-1}
$CH\ NO_{2\ 3}$	*ca.* 360 cm^{-1}
$C\ NO_{2\ 4}$	340 cm^{-1}

Buczkowski and T. Urbański [29] found the bands in 2,2-dinitropropane in both infra-red and Raman spectra: asymmetric NO_2:1588 cm^{-1}, symmetric NO_2:1367, 1342 and 1258 cm^{-1}.

Salts of nitro alkanes show a considerable deviation from the non-ionized nitroalkanes. Novikov and co-workers [7] give the frequencies of mononitro anion as follows:

$\nu(C{-}N)$	1610–1440 cm^{-1}
$\nu_{as}(NO_2)$	1285–1140 cm^{-1}
$\nu_S(NO_2)$	< 1000 cm^{-1}

Figure 11 depicts the change of frequencies when 'true' nitro compounds are transformed into their salts, according to Novikov and co-workers [7].

Conduit [14] established the influence of steric effects upon the symmetric vibrations. All dinitro derivatives of benzene and toluene which contain one nitro group strongly hindered and non-planar with the benzene ring show a splitting of the symmetric vibrations band, Table 19.

TABLE 19. Infra-red bands of sym-NO_2 in sterically hindered nitro compounds

o-dinitrobenzene shows	1368 and 1350 cm^{-1}
2,3-dinitrotoluene shows	1364 and 1346 cm^{-1}
3,4-dinitrotoluene shows	1360 and 1346 cm^{-1}
2,6-dinitrotoluene shows	1363 and 1348 cm^{-1}
3,5-dinitrotoluene shows	1356 and 1341 cm^{-1}

Unsymmetrically substituted trinitrotoluenes show a splitting of both bands, for example, 2,3,4-trinitrotoluene show asymmetric 1572, 1558 and symmetric vibration 1360, 1347 cm^{-1}. Similar bands are given by 2,3,5-, 2,3,6- and 3,4,5-trinitrotoluenes.

The asymmetric band widths reveal a regularity. The band width of an isolated nitro group is 8–11 cm^{-1} but in the presence of some hindering groups such as CH_3, C_2H_5 broadens to 19 cm^{-1}.

Varsányi, Holly and Fenichel [30] confirmed the finding of Conduit [14]

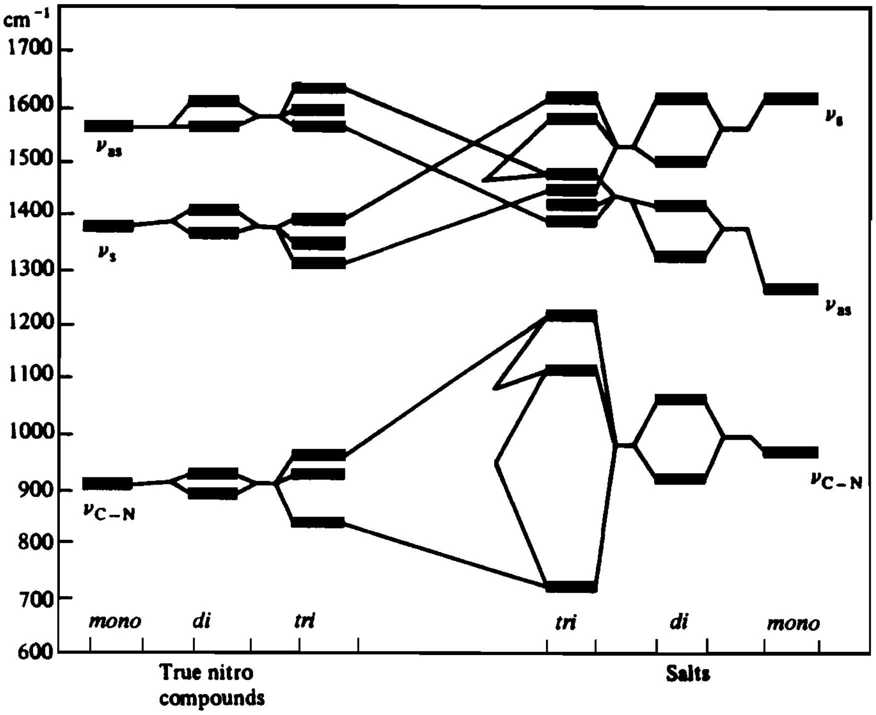


FIG. 11. Change of frequencies of aliphatic nitro compounds and their salts (according to Novikov *et al.* [7]).

and added one more band of C—N stretching vibrations in nitrobenzene, nitrotoluene and nitroanisole as being 859–851 cm^{-1}.

Steric influence was also referred to NO_2 deformation and C—N stretching vibrations in aromatic nitro compounds by Nakamura and co-workers [31]. They examined aromatic nitro compounds containing halogen substituents in various positions. They found (as anticipated) that *ortho* substitution lowered NO_2 bending and deformation modes owing to steric hindrance. This can be seen from Table 20.

TABLE 20. NO_2 bending and deformation vibration in substituted nitrobenzenes

	NO_2 bending cm^{-1}	NO_2 deformation cm^{-1}
m-chloronitrobenzene	537	733
p-chloronitrobenzene	533	740
o-chloronitrobenzene	459	686
m-bromonitrobenzene	535	728
p-bromonitrobenzene	522	732
o-bromonitrobenzene	413	685

The C —N stretching frequencies are not much influenced by substituents and in some cases the substitution increases the frequency. Thus the C —N frequency in pentabromonitrobenzene 895 cm^{-1} is much higher than in nitrobenzene 852 cm^{-1}. This is in agreement with Trotter's conclusion [32] that the C —N bonds in nitrobenzene derivatives have no resonance interaction.

T. Urbański and Dąbrowska [33a] examined infra-red spectra of mono-, di-, and trinitrophenols and particularly [33b] the action of solvents on hydrogen bonding between *o*-nitro and the phenolic group. They found that polar solvents can break a hydrogen bond. This is discussed in the paragraphs on hydrogen bonds and in the description of dinitro and trinitro phenols.

The already mentioned work of Kędzierski, Piotrowska and T. Urbański [18] on spectra of 5-nitro-1,3-oxazine revealed also the influence upon the infra-red frequency of the nitro group of its stereochemistry.

Thus the axial and equatorial NO_2 groups showed the frequencies 1556–1548 cm^{-1} and 1536–1533 cm^{-1} respectively.

A very interesting attempt was made by Boisard *et al.* [34] to use the rapid Raman spectrometry of 10 ns to study the structure of explosives immediately preceding the decomposition produced by a shock. They obtained spectra of cyclonite after the shock and the beginning of decomposition. A displacement was observed by 11 cm^{-1} of the frequency of the bond N —NO_2. This is probably due to lengthening of the bond N — N. It is expected to obtain more information in the future.

NUCLEAR MAGNETIC RESONANCE OF NITRO COMPOUNDS
(Vol. I, p. 179)

The application of nuclear magnetic resonance spectroscopy involves proton and nitrogen chemical shifts: ^{1}H-NMR and ^{14}N–NMR respectively.

Proton Magnetic Resonance

A number of aliphatic nitro compounds were examined by T. Urbański, Witanowski and co-workers [35]. The nitro group, being strongly electron attracting, decreases local electron density around alkyl protons in nitroalkanes, thus shifting their resonance signals to lower magnetic fields. The effect depends on the number of nitro groups, as can be seen in the series:

	CH_4	CH_3NO_2	$CH_2(NO_2)_2$	$CH(NO_2)_3$
δ ppm	0.23	4.28	6.10	7.52

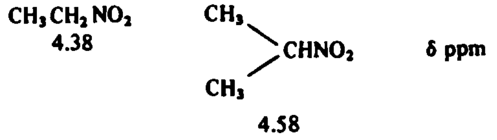
The negative inductive effect of the NO_2 group operates significantly as far as the third carbon atom in the chain. This can be seen from δ ppm data for 1-nitropropane to 1-nitropentane:

$$\underset{1.05}{CH_3} - \underset{2.04}{CH_2} - \underset{4.30}{CH_2} - NO_2$$

$$\underset{1.00}{CH_3} - \underset{1.46}{CH_2} - \underset{2.03}{CH_2} - \underset{4.33}{CH_2} - NO_2$$

$$\underset{0.96}{CH_3} - \underset{1.33}{CH_2} - \underset{1.33}{CH_2} - \underset{2.03}{CH_2} - \underset{4.30}{CH_2} - NO_2$$

Also a difference was observed between primary and secondary nitroalkanes:



$\underset{4.38}{CH_3CH_2NO_2}$ $\underset{4.58}{(CH_3)_2CHNO_2}$ δ ppm

Proton spectra have also been used for the examination of nitro alkenes such as the isomerization of nitropropenes [36]:

$$\underset{75\%}{CH_2 = CH - CH_2NO_2} \xrightleftharpoons{RONa} \underset{25\%}{CH_3 - CH = CH - CH_3} \qquad (1)$$

A number of aromatic nitro compounds, derivatives of benzene, toluene, xylenes, mesitylene and durene have been investigated by proton resonance spectra [37–41]. The nitro group was found to shift the aromatic proton resonance signals to low fields from that of benzene in the order *ortho* > *para* > *meta*.

T. Urbański, Witanowski and associates [42] found convincing proof of the hydrogen bond between the phenolic group and the *o*-nitro group through ^1H–NMR examination of dilute solutions of nitrophenols, 2,4-dinitrophenol and picric acid. Thus *o*-nitrophenol gives $\delta = 10.67$ ppm whereas *m*- and *p*-nitrophenols 4.87 and 5.14 ppm respectively.

More information on H–NMR of nitro compounds is given by Rao in his review paper [2].

Nitrogen Magnetic Resonance

Recently less attention has been dedicated to the study of proton NMR of nitro compounds and attention has been shifted to nitrogen – ^{14}N–NMR.

The first systematic study of ^{14}N–NMR of nitroalkanes has been done by Witanowski, T. Urbański and Stefaniak [43]. It led to a simple spectral differentiation between nitromethane, primary, secondary and tertiary nitroalkanes.

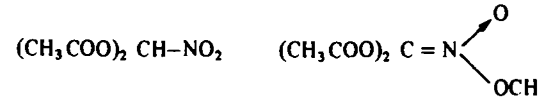
Nitromethane was taken as a primary standard for referencing nitrogen chemical shifts.

A summary of the existing data is given in Table 21 [44–46].

TABLE 21. ^{14}N–NMR of typical nitro compounds

Compounds	Nitrogen screening constants ppm
Nitromethane	0.0
$C(NO_2)_4$	+46.59
Nitrobenzene	+ 9.56
Hexanitrobenzene in CH_2Cl_2	+38.5
Nitroalkanes:	
tertiary R_3C-NO_2	*ca.* −30
secondary R_2CH-NO_2	*ca.* −20
primary RCH_2-NO_2	*ca.* − 8
gem – Dinitroalkanes $RCH(NO_2)_2$	*ca.* +20
gem – Trinitroalkanes $RC(NO_2)_3$	*ca.* +30
Aromatic nitro groups	+ 5 to +30
N-Nitro group R_2N-NO_2	+20 to +40 NO_2
O-Nitro group $R-O-NO_2$	+35 to +60

Electron attracting substituents in the nearest vicinity to the nitro group tend to increase the screening constant for the latter. Nitrogen chemical shifts differentiate clearly nitroalkanes, nitroaromatics, *N*-nitro and *O*-nitro groups. They are also helpful in distinguishing between the true nitro structure and that of an aci-nitro compound:


$(CH_3COO)_2CH-NO_2$ $\quad$ $(CH_3COO)_2C=N(\rightarrow O)OCH_3$

+ 16 ppm
nitro compound

+ 70 ppm
aci-nitro derivative

Additivity rules were found for the nitrogen chemical shifts in nitroalkanes [49].

The experiments on ^{14}N–NMR were extended to correlations of the ^{14}N chemical shifts with the infra-red frequencies of the nitro group [49b, 50] and with the Taft constants [48, 49a].

NMR spectra of nitrophenols offered a great help in examination of intramolecular hydrogen bond in β-nitroalcohols [68a] and *o*-nitrophenols [42]. The problem is discussed in the paragraph on hydrogen bond (p. 81).

A number of papers deal with the ^{14}N–NMR spectra of anions derived from mono- and polynitroalkanes. The change of structure from that of a true anion of aci-nitroalkane to that of a true nitrocarbanion was suggested in the series of anions of mono-, di-, and trinitroalkanes on the basis of the ^{14}N spectra [50]. Some data on the ^{14}N, ^{15}N, ^{13}C and ^{17}O resonance shifts were reported for nitroalkane anions [51–53] and ^{17}O for nitroalkanes [54].

The ^{14}N resonance spectra of aromatic nitro compounds [55] show inductive effects of substituents on the nitro group.

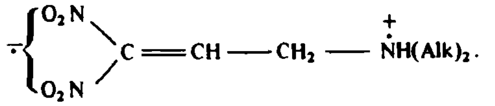
The nitrogen resonance spectra have been reported for the nitronium ion (NO_2^+) [56].

For more information and details the monographs [44–46] should be consulted.

Electron Spin Resonance

As is generally known, electron spin resonance reveals the presence of unpaired electrons. This is of course characteristic of free radicals and the most well known stable free radical is α, α′-diphenyl-β-picrylhydrazyl(DPPH) (I, 213). In the ESR spectrum it gives a narrow signal close to free spin value $g = 2.0036$ and is used for calibrating the magnetic field [2].

Unpaired electrons are also present in free radicals, radico-ions and in charge–transfer complexes. Among the latter a very prominent group is formed by polynitro compounds as acceptors and aromatic hydrocarbons mainly with condensed rings. The nature of these complexes is discussed further on p. 83. Now it should be mentioned that all CT complexes give a prominent ESR signal. More recently T. Urbański and co-workers [57] found that nitro compounds, both aliphatic and aromatic, give ESR signals if they contain a donor such as the amino group. Typical examples are nitroanilines, *m*-nitroaniline. Among aliphatic compounds 1,1-dinitropropenyl-3-dialkylamines show a strong ESR signal very likely due to the structure



These compounds can be regarded as 'internal' CT complexes, or 'autocomplexes'. A number of such complexes with nitro groups were described by Freimanis *et al.* [141].

Micro-wave Spectroscopy

Micro-wave spectroscopy has been very little used for the examination of nitro compounds. Only a few data exist on the rotational constants of NO_2 group about the symmetry axis for nitromethane [2, 7] and some derivatives of nitromethane [7].

Magnetic and Electric Birefringance

Magnetic birefringance (Cotton–Mounton effect) and electric birefringance (Kerr effect) of nitrobenzene, *p*-dinitrobenzene and 1,3,5-trinitrobenzene was recently examined by Battaglia and Ritchie [58] at 25°C and 633 nm.

The following were figures for $\Delta\chi$ molecular magnetic anisotropy:

benzene	− 64
nitrobenzene	− 96
p-dinitrobenzene	− 151
1,3,5-trinitrobenzene	− 147

Optical Rotatory Dispersion

Optical rotatory dispersion and circular dichroism of compounds with a nitro group as a chromophore was described by Djerassi and co-workers [59].

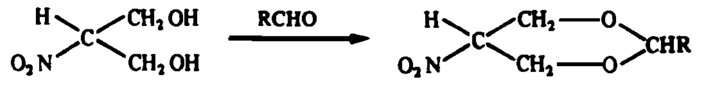
Polarisability

The electrical polarisability of nitro compounds was discussed by G.F. Wright [146]. He pointed out the behavioural peculiarities of the nitro group in electric field.

HYDROGEN BOND WITH THE NITRO GROUP (Vol. I, p. 170).

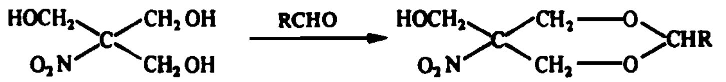
Malinowski and T. Urbański [60] advanced a suggestion that a hydrogen bond can exist between the nitro and the hydroxy group in β-nitro alcohols. This was based on the experimental fact that 2-nitropropane-1,3-diol (I) formed cyclic acetals-1,3-dioxane derivatives (II) and ketals with great difficulty, while on the contrary the triol 2-hydroxymethyl-2-nitro-propane-1,3-diol (III) forms the corresponding cyclic acetal (IV) and ketal with great ease.

These facts were rationalized in terms of the hydrogen bonds between the nitro and the hydroxy groups: Ia and IIIa



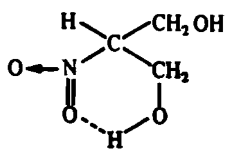
I II

(2a)

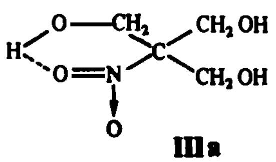


III IV

(2b)



Ia



IIIa

The presence of the intramolecular hydrogen bond between NO_2 and OH groups or NO_2 and NH groups was later confirmed by the author [61] on the basis of ultraviolet spectra of *ca.* 50 β-nitroalcohols, diols and β-aminomethyl-β-nitroalcohols and the comparison of their spectra with those of nitroalkanes.

The conclusion of T. Urbański was questioned by Ungnade and Kissinger [62] who admitted only a very weak hydrogen bond between β-nitroalcohol and chloroform used as a solvent. Schleyer and co-workers [63] have criticized the conclusions of Ungnade and Kissinger thus supporting the view of T. Urbański. Also Krueger and Mettee [64] confirmed the existence of the discussed hydrogen bonding. Two earlier papers [65, 66] referred to infra-red spectra of β-aminoalcohols and the authors rationalized the results in terms of the hydrogen bond between NO_2 and OH groups.

Final proof of the existence of the hydrogen bonding between NO_2 and OH groups in β-nitroalcohols was given by further experiments of T. Urbański and co-workers. The following methods were used in their experiments: measurement and calculation of dipole moments [67], ultraviolet, infra-red (including overtone region), NMR spectroscopy [68a, b].

A number of nitrophenols, nitroanilines, nitronaphthols etc. have been examined through ultraviolet spectroscopy, the point of acid–base equilibria, solute–solvent effect and internal hydrogen bonding and partly reviewed [2, 69, 70] Lutskii and Gorokhova [71] have calculated and interpreted the electronic spectra of nitrophenols by a LCAO SCF MO method in Pariser–Parr–Pople approximation. On scrutinizing the experimental electronic spectra (both ultraviolet and visible) of nitrophenols in different solvents (cyclohexane, absolute and 20% aqueous methanol) Skulski [72] has come to the conclusion that *o*-nitrophenol is strongly chelated in cyclohexane solution, but not appreciably in methanolic and probably not at all in aqueous methanol. Also by measuring dipole moments in dioxane and benzene he obtained [73] valuable information on the stability of the intramolecular hydrogen bond to the action of dioxane and other active solvents.

The effect was examined [74] of surfactants on the visible spectra of nitrophenols in 3% aqueous ethanol and interactions between the nitrophenols and micelles. The electron absorption spectra of dinitroanilines have been discussed [75] in terms of energy and intensity of lowest energy absorptions, the intramolecular hydrogen bond extension of the π electron conjugated system etc.

T. Urbański and Dąbrowska [33b] examined infra-red spectra of several mono-, di- and trinitrophenols and established the influence of the solvent on the hydrogen bond between the *o*-nitro and phenolic groups. It was found that polar solvents can break the intramolecular hydrogen bond.

Reeves and co-workers [76] correlated the change in the chemical shift of NMR spectra caused by formation of an intramolecular hydrogen bond in *o*-substituted phenols including *o*-nitrophenol, 2,4-dinitrophenol, 1-nitro-2-naphthol, 2,4-dinitro-1-naphthol etc.

Final evidence of intramolecular hydrogen bonding in nitrophenols and hydrogen bonding in nitrophenols was given by T. Urbański, Witanowski and co-workers [77] by examining their NMR spectra. The values of δ calculated for infinite dilutions for OH groups and the infra-red frequencies are shown in Table 22.

TABLE 22. Chemical shifts δ_{OH} ppm and infra-red frequencies in cm^{-1} for nitrophenols

Compound	δ_{OH} ppm	IR bands cm^{-1}
o-Nitrophenol	10.67	3250
2,4-Dinitrophenol	11.12	3210
2,5-Dinitrophenol	10.76	3270
2,6-Dinitrophenol	11.41	3170
Picric acid	9.16	3100
m-Nitrophenol	4.87	3615
p-Nitrophenol	5.14	3615

The infra-red data [30a] refers to solutions in carbon tetrachloride. They show a considerable difference between *ortho* nitro phenols and *m*- and *para*-nitro derivatives.

A number of authors [78–81] examined the intramolecular hydrogen bonds between NO_2 and NH_2 in *o*-nitroaniline.

CHARGE–TRANSFER COMPLEXES (CT-COMPLEXES) OR ELECTRON–DONOR–ACCEPTOR COMPLEXES (EDA-COMPLEXES) (Vol. I, p. 220).

As pointed out in Vol. 1, trinitrobenzene and its derivatives possess the ability to form addition compounds, especially with aromatic hydrocarbons composed of condensed rings, such as naphthalene, anthracene, phenanthrene, acenaphthene etc. Addition compounds of picric acid have been known since 1858 [82] and those of sym-trinitrobenzene since 1882 [83]. Complexes of sym-trinitro-benzene with aromatic amines were also described in 1882 [84].

Currently problems connected with CT or EDA complexes form one of the topics of physical–organic chemistry. A few excellent monographs and review articles have appeared [85–90]. After the remarkable work of Briegleb, Weiss, Brackman and other authors (Vol. I, p. 220) the most important treatment of the nature of bonds keeping donor and acceptor together, was given by Mulliken [91] on the basis of quantum mechanical assumption of the electron transfer from the donor to the acceptor.

Here are the main points deduced by Mulliken. The electronic ground state wave functions of the complex ψ_N are a combination of a 'no-bond' wave function ψ_0 and one or more 'dative bond' functions ψ_1, ψ_2 etc.:

$$\psi_N = a\psi_0 + b\psi_1 + c\psi_2 + \ldots,$$

where a, b and c are coefficients with $a > b > c$.

The no-bond function includes the electronic energy of the component molecules, plus terms representing the effect of dipole interactions, dispersion forces, hydrogen bonding and other intermolecular forces. The dative bond functions represent states where an electron has been transferred from the donor molecule to the acceptor, introducing electrostatic interactions and forming a weak covalent link between the resulting radical ions:

$$\begin{tikzcd}
A\,D \arrow[r, leftrightarrow] \arrow[d, "h\nu"] & A^- + D^+ \\
A^- + D^+ \arrow[r, phantom, "\rightleftharpoons"] & A^- \leftrightarrow D^+
\end{tikzcd}$$

EDA Complex

Excited states with a dative structure as the main contributor, have the same form with the coefficients varied to give predominance to the dative bond contribution.

The Mulliken treatment provided the theoretical basis for interpretation of spectroscopic and formation constant data and initiated research on semiconductivity and magnetic properties of molecular complexes.

According to McGlynn [85] and Briegleb [87] the complex addition compounds should be called 'EDA-complexes' for Electron–Donor–Acceptor–Complexes and the term 'Charge–Transfer' should be reserved for the absorption band characterizing the complex. The symbol $h\nu_{CT}$ is given to the energy of the 'charge–transfer band' characterizing the complex. Thus the term 'Charge–Transfer', according to Briegleb, is reserved in this particular instance.

According to Dewar and Lepley [92] the following are CT-bands of complexes of sym-trinitrobenzene and hydrocarbons (Table 23). Also they calculated the energy E_m of the highest occupied *MO*.

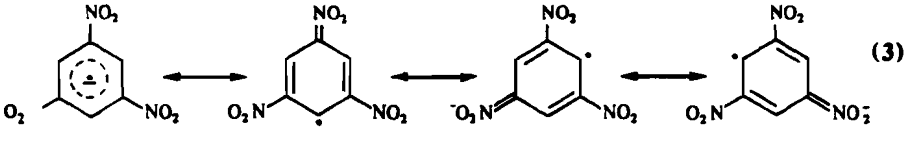
TABLE 23. The CT-bands of complexes of sym-trinitrobenzene and hydrocarbons

Hydrocarbon	CT-band ν nm	E_m
Benzene	284	1.000
Naphthalene	365	0.618
Acenaphthylene	353	0.637
Anthracene	460	0.414
Naphthacene	520	0.294
Phenanthrene	370	0.605

The figures brought to coordinates – E_m against ν – form a straight line.

A very important feature of EDA-complexes is the fact that in the magnetic field they show the existence of an unpaired electron, i.e. signals in the electron spin resonance apparatus.

Briegleb and Czekalla [86] depicted the formation of radical-ions of trinitrobenzene in the following way (3):


(3)

The electron affinity of trinitrobenzene which characterizes the ability of the compound to form charge–transfer complexes is not very high and is estimated to be equal to 0.6 eV, whereas stronger electron acceptors such as tetracyanethylene and chloranil show values of 1.6 and 1.35 eV respectively [86].

The Mulliken treatment provided a simple classification of molecular complexes according to the type of orbitals involved in charge–transfer [93]. The complexes of nitro compounds with hydrocarbons belong to π–π complexes i.e. π-donors and π-acceptors.

For maximum charge–transfer interaction the relative orientations of the two molecules must provide maximum overlap of the filled donor orbital and the vacant acceptor orbital. This is known as Mulliken's 'Overlap and Orientation principle' [94].

X-ray examination of π–π molecular complexes shows that the crystals of the complexes are formed from stacks of alternate donor and acceptor molecules – in agreement with theoretical analysis of Mulliken.

This was described by a number of authors (Vol. I) for example, Powell and Huse, Rapson, Saunder and Stewart and Wallwork [95] subjected a few complexes of *s*-trinitrobenzene to X-ray analysis. Wallwork concluded that the structure can be summarized and plane-to-plane packing of the components. The relative dispositions of the components are such as to allow the maximum degree of overlap between their molecular π-orbitals. Figure 12 gives a diagrammatic presentation of the complexes of sym-trinitrobenzene with naphthalene, and Fig. 13 – with anthracene [96].

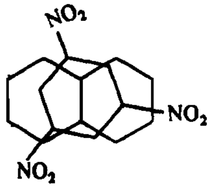


FIG. 12. CT – complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96]).

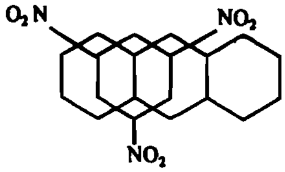


FIG. 13. CT – complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96]).

Particular cases of EDA complexes are those of nitrophenols and bases, for example, dinitrophenols with aniline described by Zeegers-Huyskens [96a], mono-, di-, and trinitrophenol with hexamethylenetetramine of Vagaonescu and Ionescu [96b]. The complexes show the presence of hydrogen bonds in addition to the existence of π–π complexes. High nitrated aromatic compounds have been used for the identification of multi-ring aromatic hydrocarbons and various amines. Thus Willstätter and M. Fischer [97] used styphnic acid, an acceptor to detect porphyrins, and later a few papers were added on similar detection of chlorophyll and other porphyrin-like molecules with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone [98–100]. Some alkaloids and drugs can be detected and subjected to quantitative analysis by measuring the intensity of the charge–transfer band produced in the spectrum of complexes with 1,3,5-trinitrobenzene or picric acid [101, 102].

Also highly nitrated compounds can be detected and identified by means of donors, such as hydrocarbons. Their identification was suggested by the method of thin-layer chromatography [103]. A method of rapid detection, of explosives such as TNT, TNB, Picryl chloride, *m*-DNB, Tetryl in the form of charge–transfer complexes with aromatic amines, such as aniline, dimethylaniline, toluidines, anisidines, naphthylamines, benzidine etc. was developed by Dwivedy *et al.* [104]. The authors used for identification thin-layer chromatography establishing R_f values for model complexes.

An original approach to the stereostructure of complexes on the basis of infra-red spectra was given by Severin [105]. He examined the complexes of sym-trinitrobenzene with phloroglucinol or nitrophloroglucinol and of picric acid with phloroglucinol and came to the conclusion that the approach of the acceptor molecule can be sterically hindered if the donor molecule is non-planar. Hence complex formation is difficult as the non-planarity increases the distance between the components. For example, *trans*-stilbene forms a picrate, but the *cis*-isomer does not. The planar molecule of 2-phenylnaphthalene also forms a picrate, while its non-planar isomer, 1-phenylnaphthalene, fails to do so.

A number of papers have appeared which describe absorption spectra of charge–transfer complexes in solutions without however isolating the actual complexes.

Thus Foster and Thomson [106] examined complexes of *p*-phenylenediamine and its *N*-methyl derivatives, and bis(dimethylamine) derivatives, of diphenyl and stilbene with 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3- and 1,4-dinitrobenzene and 1,3,5-trinitrobenzene. Similarly Wacławek and Hurwic [107] described complexes formed in solutions by 1,3,5-trinitrobenzene with pyridine, picolines, aminopyridines and cyanopyridines. They also used dielectric titration, refractive index and density measurements to establish the formation of the complexes. Aliphatic nitro compounds can also be electron acceptors. Thus Lewańska and Lipczyńska [108] established the existence of a complex of ter-nitrobutane with dimethylaniline in molar proportion 1:1 by measuring electronic spectrum of solutions with different proportions of the donor and acceptor, according to the method of constant dilutions of Job [109].

Hammond and Burkardt [142] described the electron accepting properties of tetranitromethane. They came to the conclusion that tetranitromethane interacts only weakly with aromatic hydrocarbons and does not form isolable complexes.

Hetnarski [110] in a number of papers has described a new donor – ferrocene. It gives EDA complexes with sym-trinitrobenzene, picric acid, picryl chloride while using Job's method [109] to establish the ratio between the acceptor and donor.

More recently T. Urbański, Hetnarski and Południkiewicz [111] established that nitrate esters form EDA complexes with a strong donor – *N,N'*-tetramethyl-*p*-phenylenediamine. Particularly interesting are nitrate esters with five or six ONO_2 groups, such as D-arabitol pentanitrate, D-mannitol and D-sorbitol hexanitrates. A particular stereochemistry of such complexes was suggested with nitrate esters coiled in pseudo-rings. Complexes of erythritol tetranitrate with biologically important pyrimidine and purine bases were examined by T. Urbański, Wacławek and Pobłocka [112]. The ratio donor:acceptor was established by examining NMR spectra.

T. Urbański, Krasiejko and Południkiewicz [113] suggested using *N,N'*-tetramethyl-*p*-phenylenediamine to detect nitrate esters: a magenta colour makes the detection easy.

Like most EDA complexes, those of sym-trinitrobenzene, for example, with *N,N*-dimethylaniline show a semiconducting property [114].

X-Ray Structure

A considerable number of X-ray examinations of nitro compounds have been done over the last two decades. They will be given in the description of particular compounds. However, the following are reviews which should be mentioned: X-ray analysis of aliphatic nitro compounds, nitrate esters and nitramines were described by Novikov and co-workers [7], nitramines by G. F. Wright [115], polynitroaromatic addition compounds by Hall and Poranski [116]. The X-ray crystal structure of EDA complexes – by Prout and J. D. Wright [88] and Foster [90].

THERMOCHEMISTRY

Thermochemical data of explosives will be given in the description of particular compounds. General problems of thermochemistry of nitro compounds was given in the monograph by Lebedev, Miroshnichenko and Knobel [117]. In recent years a considerable number of contributions have been given by Pepekin and co-workers [118] on such problems as the enthalpy of formation of nitro and nitramino compounds and nitrate esters and enthalpy of detonation. Also Pepekin and co-workers [119] contributed considerably to the solution of problems of the energy of dissociation of the bond $C-N_3$.

A very important review article on thermal analysis of explosives was given by Collins and Haws [140]. The results of thermal analysis will be described in properties of particular compounds.

MASS SPECTROGRAPHY

A number of papers have appeared on the fragmentation of nitro compounds by mass spectrography. They were reviewed by Beynon [120] and recently by Khmel'nitskii and Terentiev [121] therefore only main outlines will be given here. Three main molecular ions have been found: $M-O^+$, $M-NO^+$ and $M-NO_2^+$. The first one was present in a small yield 1–2%. There are two schools of thought, as far as the mechanism of rearrangement of the molecular ion prior to its dissociation. According to some authors [122] the molecular nitro-ion is first rearranged into a nitrite. McLafferty and Bursey [123] found a marked distinction between compounds having *meta* and *para* positions of the nitro group relative to other substituents.

Beynon, Saunders and Williams [122], Fields, Meyerson and co-workers [124] compared mass-spectra of isomeric dinitrobenzenes (Table 24) and came to the conclusion that *meta* and *para* isomers give similar fragments, whereas *ortho* differ considerably.

The fragmentation of negatively charged molecular ions of mono- and dinitrobenzenes does not differ from that of the positive ions [125, 126].

Meyerson *et al.* [127] examined the fragmentation of sym-trinitrobenzene. A much more complicated picture appeared from the spectrum with one particular feature: the most prominent is the elimination of NO_2 as the first step of the fragmentation.

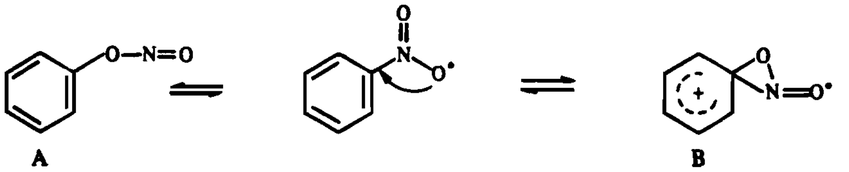
Experiments with isomeric nitrotoluenes show that the fragmentation of *meta*- and *para*-isomers is similar to that of nitrobenzene [122].

Both isomers are characterized by the high presence, *ca.* 70%, of the molecular ion, while nitrobenzene shows 49% and *o*-nitrotoluene only 25%. The

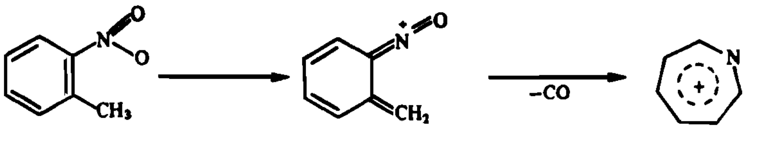
TABLE 24. Intensity of the peaks of mass-spectra of isomeric dinitrobenzenes in percentages

Ions	Isomers of DNB *ortho*	*meta*	*para*
M^+	6.98	11.00	10.30
$M-O^+$	0.24	0.63	0.57
$M-NO^+$	0.07	0.21	0.34
$M-NO_2{}^+$	0.41	4.76	4.12
$M-NO_2{}^+$	0.03	0.04	0.09
$M(NO)NO_2{}^+$	1.66	5.82	3.64
$M(NO_2)_2{}^+$	3.84	11.20	9.18
$M-NO_2+HNO_2{}^+$	2.03	10.80	11.30
NO^+	26.70	17.20	21.30

spectrum of *o*-nitrotoluene shows a high peak with a mass of 120 which is not present in *meta*- and *para*-isomers. According to Beynon *et al.* [122] it corresponds to the ion $M-OH^+$ with the structure according to scheme (5)



(4)



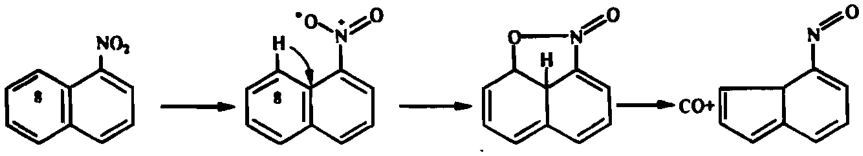
(5)

The ion 20 is losing CO to be transformed probably into the azatropilium ion 92. The mass spectra of *m*- and *p*-nitrotoluenes yielded only $M-NO^+$ and $M-NO_2^+$ ions. Nitroxylenes and polynitrotoluenes yielded ions $M-OH^+$ [122].

Mass spectrum of TNT yielded ion $[(M+H)-OH_2]^+$ [128].

The peak $(M-OH)^+$ is present in the mass spectra of all three nitroanilines [122, 129].

Benoit and Holmes [130] examined a number of *o*-nitro compounds, such as *o*-nitroanisol, *o*-nitrobenzoic acid, *o*-nitrobenzamide etc. to study the *ortho*-effect. They came to the conclusion that two *ortho*-effects exist. One is marked by the migration of hydrogen from one substituent to another. The second effect consists in migration of an atom or a group of atoms from the substituent of a vacant place in *ortho* position. Particular attention is now being paid to elucidating different features of the *ortho* effect. Among interesting facts a similar effect was recorded in *peri*-position in 1-nitronaphthalene [131, 132]. The following mechanism was rationalized by labelling position 8 of the naphthalene ring with ^{13}C [133]:



(6)

Nitroalkanes: nitromethane, nitroethane and nitropropanes were examined by Collin [134].

ELECTROCHEMICAL PROPERTIES

Galvanic Cells

Nitro compounds and metals as reducing agents can form galvanic cells [134]. Particularly interesting are results with *m*-dinitrobenzene [135]. The system *m*-dinitrobenzene and magnesium gave a rather high yield of 160 wh/kg through the reaction:

$$R(NO_2)_2 + 4H^+ + 4e \longrightarrow R(NHOH)_2 + H_2O \qquad (7)$$

in a neutral medium.

Photoconductivity. It has been found that the conductivity of nitrobenzene increases when irradiated with ultraviolet light [136]. This will be discussed in the paragraph on the photochemistry of nitro compounds.

Lasers. Chelates of europium with some aromatic nitro compounds with phenolic and aldehydic function can be used to produce laser beams [137].

BIOLOGICAL ACTIVITY OF NITRO COMPOUNDS

Nitro compounds possess strong biological activity. Moncrieff [138] has given a first monograph of such properties as sweet and bitter or pungent taste, musk odour. A review by Venulet and Van Etten [139] described the biochemistry and pharmacology of nitro compounds and included a description of antibiotics containing the nitro group such as naturally occurring nitro compounds, toxic substances with their practical use as insecticides, molluscicides, fungicides and herbicides. A separate chapter is dedicated to the toxicity of commercially important nitro compounds.

Reactive aromatic nitro compounds were successfully used as antitumour agents. Such is chlorodinitrobenzene [143] and some 2,4-dinitrophenyl derivatives, such as 5-aziridino-2,4-dinitrobenzamide [144].

The toxicity of nitro compounds was discussed in Vol. I in the description of particular compounds. This method will be followed in the present volume: any novel information on the toxicity of compounds, were available, will be given in the description of the compounds.

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CHAPTER 4

REACTIVITY OF AROMATIC NITRO COMPOUNDS

(Vol. I, p. 192)

A great number of reactions of nitro compounds were described in the well known monograph edited by H. Feuer which forms a part of the monographs edited by S. Patai [1]. Reference will therefore be made to these and some other books and only the most important and more recent papers will be given here.

SUBSTITUTION (HETEROLYTIC AND HOMOLYTIC)

It is well known that heterolytic substitutions occur through 'electrophilic' and 'nucleophilic' attacks produced by cation E^+ ('electrophile') and anion Nu^- ('nucleophile') respectively. Homolytic substitutions involve the action of uncharged free radicals.

In electrophilic and nucleophilic substitution of aromatic nitro compounds different directing effects are dictated by electron distribution. The simple case of nitrobenzene π-electron distribution is given in diagram Fig. 14a [2], and the free valence of aromatic cations of nitrobenzene $C_6H_5NO_2^+$ is given in Fig. 14b [3].

Both diagrams show that electrophilic substitution should occur mainly in *meta* position, whereas the nucleophilic one should yield mainly *ortho* and *para* substituted products.

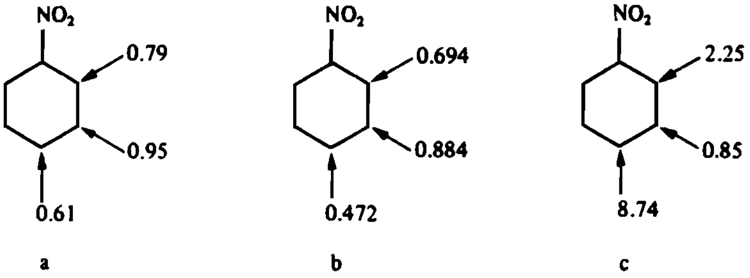


FIG. 14. Nitrobenzene: (a) π-electron density (see also Fig. 7); (b) free valencies; (c) localization energy.

Another approach consists of the calculation of relative rates for substitution from the atom localization energies of Wheland. It gives a more qualitative insight. However in the instance of homolytic reactions at 80°C the relative reaction rates are better approaching the experimental results (Fig. 14c).

ELECTROPHILIC SUBSTITUTION

A few monographs have been dedicated to the description of electrophilic substitution of nitro compounds in general [2, 5–7] and a review has been published on the subject [8]. The mechanism of nitration was discussed in Chapter II. Nitration with NO_2^+ containing agents belongs to the mechanism SE 2 as already mentioned in Chapter II.

Diagrams – Fig. 14a–c – shows that substitution can occur not only in *meta*, but also in *ortho* and *para* positions. According to the diagrams it should be expected that the proportion of *ortho* isomer should be superior to that of the *p*-dinitrobenzene. Indeed this is in agreement with the experiment: the proportion of *o*-dinitrobenzene is larger and at high temperature of nitration much larger than that of *p*-dinitrobenzene (Vol. I, p. 243, Tables 38 and 39).

Also in the homologues of benzene the influence of alkyl groups should not be neglected, their directing influence being *ortho* and *para*.

NUCLEOPHILIC ADDITION AND SUBSTITUTION (Vol. I, p. 197)

One of the characteristic features of aromatic nitro compounds, particularly those with two or more nitro groups is their ability to react with bases and in many instances the reaction is accompanied by an intense colour. The colour had caught the attention of chemists by the late nineteenth century and initiated a considerable amount of research on the nature of the formed substances. Thus considerable literature appeared on reactions known as Janovsky or Jackson–Meisenheimer or Meisenheimer reactions which are discussed later. They are nucleophilic reactions and are not only of theoretical but also of practical importance. Thus the Janovsky reaction became an important analytical method, and reactions of di- and trinitrobenzene and their homologues with bases, are of great importance in the problem of the safety of manufacture and of the stability of these nitro compounds.

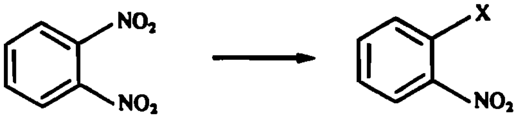
The reactions of nitro compounds with bases are nucleophilic reactions and recently have received much attention. Numerous monographs include chapters on nucleophilic substitution of nitro compounds and review articles have been published. Such are the excellent reviews by de Boer and Dirkx [9], Hall and Poranski [10]. References in [9] are brought up to 1966, and it seems appropriate to complete the list of review articles by mentioning the later review papers: Challis [11], Buncel and co-workers [12], Miller [13], Pietra [14], Buck [15], Crampton [16], Strauss [17], Bernasconi [18], Sekiguchi and Yuki [19], Makosza [20], Kornblum [144], Bolton [174], Blumenfeld and co-workers [178].

Two excellent monographs appeared recently on analytical problems of explosives. Gawargious [179] gave a description related to the nitro group. Yinon and Zitrin [189] tackled a wide range of analysis of various explosives.

However the analytical problems are outside the scope of the present book.

NUCLEOPHILIC DISPLACEMENT OF NITRO GROUP

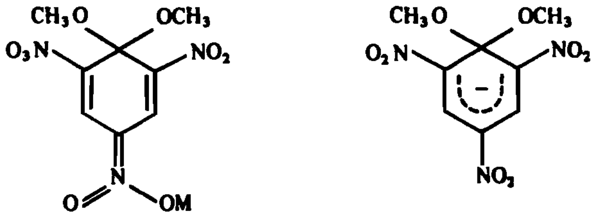
Nucleophilic displacement of aromatic nitro group was recently reviewed by Beck [234]. An attention was drawn to his own work and that of Cadogan and co-workers [225, 226], e.g.:



X = $PO/OC_2H_5/_2$,
$PO/CH_3/OC_2H_5$,
$PO(C_6H_5)_2$

JACKSON–MEISENHEIMER REACTION (OR MEISENHEIMER REACTION) AND σ-COMPLEXES

As early as 1895 Lobry de Bruin [22] described a red solid which he isolated from the reaction of 1,3,5-trinitrobenzene with potassium hydroxide in methanol. V. Meyer [23] suggested this to be a complex compound. Hantzsch and Kissel [24] rationalized that the complex might be a potassium salt of aci-form of one nitro group. Jackson and Gazzolo [25] suggested in 1900 two structural formulae for the sodium salt obtained by acting with sodium methoxide on 2,4,6-trinitroanisol – Fig. 15a. Meisenheimer [26] (probably unaware of Jackson's paper)



M = Na, K

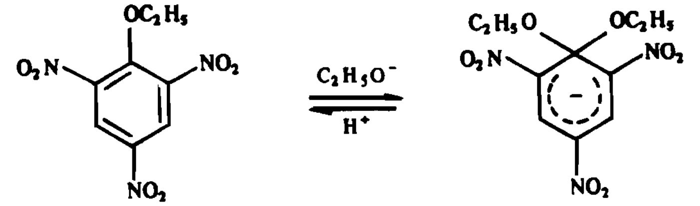
(a)

(b)

FIG. 15. Jackson–Meisenheimer σ complexes (a) former, (b) current method of writing.

suggested the same formula for potassium salt. Jackson and Earle [27] supplied analytical proof of the structure.

Jackson–Meisenheimer compounds are now recognized as σ-complexes. Currently their mode of writing is given in Fig. 15b, and the formation presented in diagram (1):



(1)

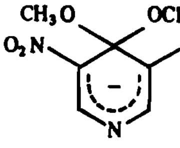
This can be classified as a SNAr mechanism.

Attention should be drawn to the fact that the reaction is reversible and under the action of an acid, the starting nitro compound is formed.

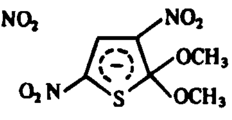
Naphthalene analogues of Jackson–Meisenheimer complexes were described [28, 42] and 9-anthracene derivative has already been discussed by Meisenheimer [26].

A few heterocyclic Jackson–Meisenheimer complexes were recorded, viz.: I [29]; II [30]. Vickery [31a] rationalized the structure of the complex (III) obtained in 1883 by Lobry de Bruin [31b] while acting with potassium cyanide on *m*-dinitrobenzene.

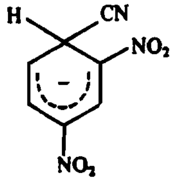
Similar σ-complexes (IV) can be obtained by acting with CH_3O^- on picramide and its derivatives [32–34, 37].



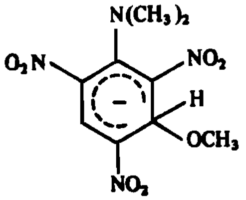
I



II



III



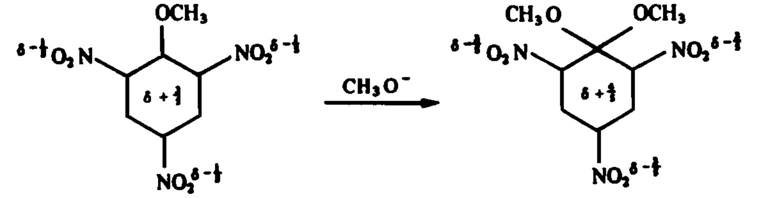
IV

Gold and Rochester [32] and Pollitt and Saunders [35] examined electronic spectra, Dyall [36] infra-red spectra of σ-complexes. NMR spectra were studied in the pioneering work of Crampton and Gold [37], the works were reviewed by Hall and Poranski [10] and Crampton [38]. More recent works were done by Norris [39] and Epiotis [40]. Kinetic studies of σ-complexes were made by a number of authors [41, 42] and thermodynamic control by Fendler and coworkers [43]. Bernasconi [18] reviewed the work on kinetic behaviour of σ-complexes.

In their recent work Crampton and Gibson [33] used a modern technique of stopped flow and T-jump spectrometry in their study of the reaction of *N*-alkyl picramide and CH_3O^-.

All of these works confirmed in principle the structure of Jackson–Meisenheimer complexes. It was also supported by X-ray analysis by Simonetta and co-workers [44] and Ueda and co-workers [45] with one correction: the length of the bonds between carbon atoms 2–3 (and 5–6) is relatively short (1.35 Å), close to the length of the olefinic bond. Subsequently the original formula – Fig. 15a – with quinoid structure should be preferred. Crampton and Gold [37b] arrived at a similar conclusion.

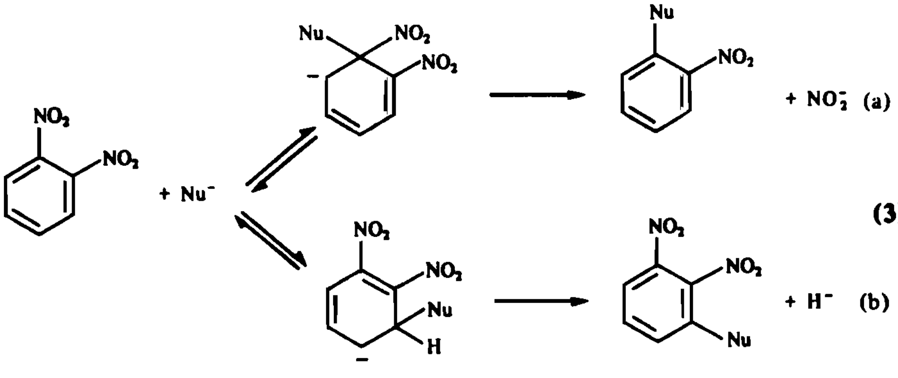
However, Heilbronner, Zollinger and co-workers [46] came to the conclusion that the existing formula of Jackson–Meisenheimer complexes is insufficiently exact in the light of the present theories of molecular orbital calculation. By using HMO method a shifting of π-electrons by the nitro groups should be considered. Thus the reaction of trinitroanisol with the methoxy anion can be depicted by diagram (2):



(2)

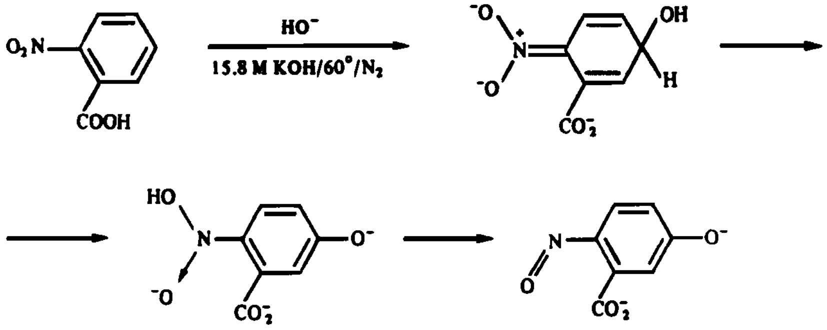
An interesting and novel approach to the Addition–Rearrangement–Elimination mechanism of tautomeric migration was recently reviewed by Minkin, Olekhnovich and Zhdanov [217]. The review also contained *N,N'* transfer of 2,4-dinitro- and 2,4,6-trinitrophenyl groups in a series of benzamidine derivatives [218, 219] and a description of previously unknown dipolar Meisenheimer spiro complexes. The authors point out the importance of this work to the design of new tautomeric systems with short living intermediate species.

Jackson–Meisenheimer type complexes can become intermediates which are further transformed into products of nucleophilic attack. Bowie [47] has produced diagrams as follows:



(3)

An interesting reaction of converting nitrobenzene into *p*-nitrosophenol [48] was now rationalized in terms of the formation of Jackson–Meisenheimer intermediate, according to scheme (4):

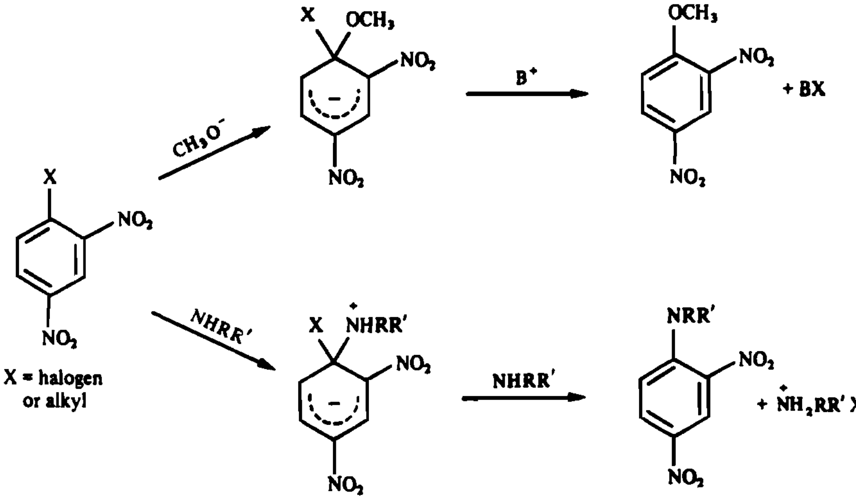


(4)

Practical Significance and Application of Jackson–Meisenheimer Reaction

The Jackson–Meisenheimer reaction is of considerable theoretical and practical significance for analytical and preparatory work in the laboratory and in industry. The latter refers to replacing halogen or alkoxy groups in nitroaromatics by acting with bases and it received full attention in Vol. I (pp. 197, 453, 461, 467, 484, 545, 547, 549, 559, 563, 571) and Vol. III (pp. 47, 61).

The reaction should be rationalized in terms of the formation of intermediate σ-complexes [21, 42]:



(a)

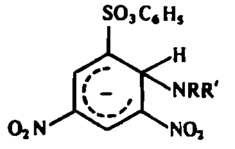
(5)

(b)

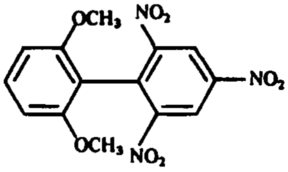
A free-energy contour diagram of reaction (5a) is given in a review paper [18].

Fluoro-2,4-dinitrobenzene is extensively used in the determination of *N*-terminal groups in peptides. A number of other nitro compounds reacting with nucleophiles are in use in biochemical work. A very wide description of the structure, kinetic properties and equilibrium of Jackson–Meisenheimer complexes was recently given by Terrier [223]. For review see [50].

J. Urbański [51] developed a nucleophilic colour reaction of dinitroarenesulphonic esters with primary and secondary amines and quaternary ammonium hydroxides. The reaction was originally used to determine small quantities of epoxy groups in polymers. The coloured products possess the structure of σ-complexes, for example V:



V



VI

Jackson–Meisenheimer complexes can serve in obtaining nitro derivatives of diphenyl. An original approach to this type of reaction was given by Wennerström [52]. He reacted a derivative of phenylsilver with 1,3,5-trinitrobenzene in the presence of pyridine. The oxidation of the σ-complex yielded compound VI.

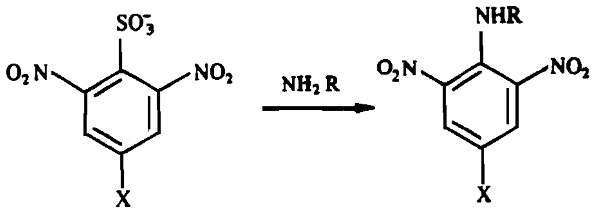
REACTION POTENTIAL MAP (RPM)

The calculation of the Reaction Potential Maps (RPM) [215] is a new kind of molecular reactivity index which is very helpful in elucidating the site selectivity observed in some chemical reactions. This was a development of the original calculation of electrostatic potential maps (EPM) by Bonaccorsi and co-workers [216].

The RPM method was proposed by Klopman *et al.* [215] to elucidate the reaction of ambient nucleophilic agents such as S CN$^-$ with hard and soft electrophiles: picryl fluoride and iodide respectively. The products contain the groups C–NCS and C–S CN respectively.

MYCELLAR NUCLEOPHILIC REACTIONS

Bunton and co-workers [53] made a significant contribution to reaction (6, X = halogen) by introducing cationic surfactants (detergents) which effectively catalysed the reaction of dinitrohalobenzenes with nucleophiles in aqueous solution by forming cationic mycelles. Cetyltrimethylammonium bromide and chloride (CTABr and CTACl) were used. Thus Bunton and co-workers [54] reported that the reaction of 2,4-dinitrofluorobenzene with $C_6H_5O^-$ and $C_6H_5S^-$ was catalysed by CTABr by factors 230 and 1100 respectively. Also the reaction of arene sulphonates with amines can be catalysed by cationic mycelles [55] (6):



$X = NO_2, CF_3$

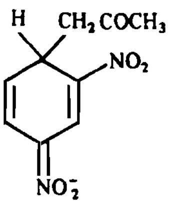
(6)

It should be pointed out that the reaction is inhibited or unaffected by anionic surfactants.

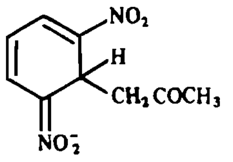
JANOVSKY REACTION (Vol. I, p. 207)

The Janovsky reaction became an important analytical test which could be used to detect both reagents: di- or trinitro-compounds or ketones and aldehydes. The modification of the reaction consisting in the use of *m*-dinitrobenzene as a test for 17-ketosteroids is sometimes called the Zimmerman reaction [15, 56].

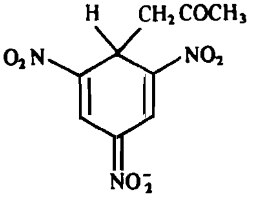
The Janovsky reaction was reviewed by Hall and Poranski [10], Buck [15], Strauss [17] and more recently by Gitis and Kaminskii [57]. The structure given in Vol. I, p. 209 is now regarded as incorrect. Instead formulae VIIa, VIIb and for 1,3,5-trinitrobenzene VIII (see also Vol. I, pp. 210–211) are now accepted. They were suggested by Hantzsch and Picton [58] as early as 1909 and more proof was given in their favour by Gitis and Kaminskii [59], Foster and Fyfe [60], Severin and Schmitz [61] and Kimura [62].



VIIa



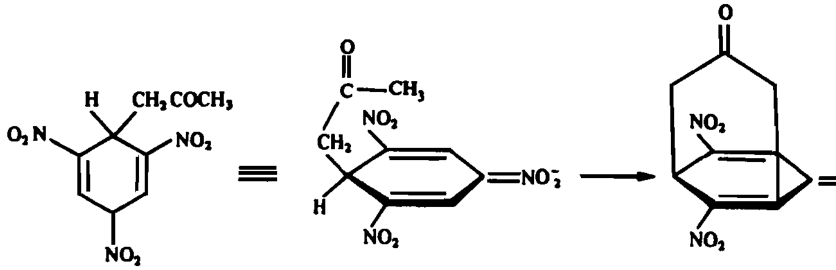
VIIb



VIII

Similar to the reaction by Jackson–Meisenheimer the formation of compounds VII–VIII is reversible and acids reproduce the substrates.

These compounds however form the first step of the Janovsky reaction. They can further react to yield bicyclic products (IX) according to Strauss and Schran [17, 63], Kohashi, Ohkura and Momosa [64] (7)



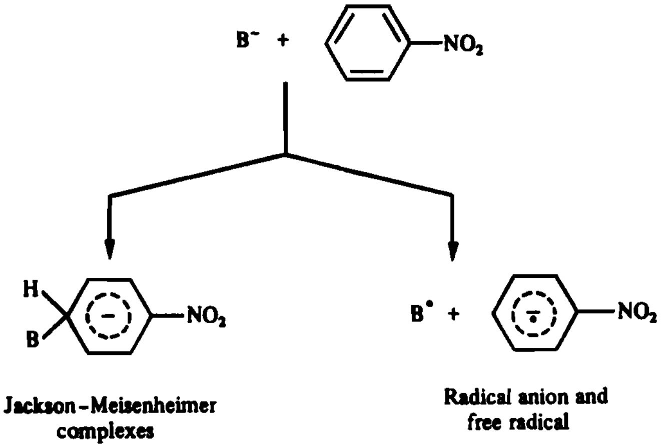
IX

(7)

The mechanism of formation VII and IX was rationalized by Sosonkin and co-workers [65] using ultraviolet, infra-red and ESR techniques.

ACTION OF BASES IN NUCLEOPHILIC REACTIONS OF NITRO COMPOUNDS

Nitro compounds can react with carbanion through the nucleophilic mechanism. Carbanions (as well as radical anions and free radicals) can be formed by the action of strong bases on nitrocompounds. Russell and co-workers [66] presented it in scheme (8):



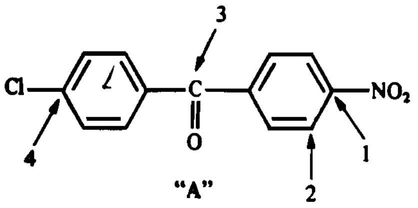
(8)

Mąkosza and Jawdosiuk [67] have found that nitrobenzene can react exothermally with nitriles in the presence of such bases as NaOH, NaNH$_2$ and CH$_3$ONa and in various solvents. Substitution in *para* position can occur. The yield was greatly influenced by the solvent. The highest (15%) was in liquid ammonia and THF at −60 to −30°C.

Mąkosza [20, 68] developed a new two phase nucleophilic reaction which consists in the use of quaternary salt of a cation (Q$^+$) – most frequently triethylbenzylammonium (TEBA) – chloride suggested originally by Jarousse [126]. The cations of TEBA are present in the aqueous phase containing a concentrated solution of NaOH (usually 50%), whereas organic phase, inmiscible in water, contains the nitro compounds and a nitrile, for example 2-phenylpropionitrile. The reaction is now known as 'Jarousse–Mąkosza' or 'Mąkosza' reaction.

Thus *p*-chloronitrobenzene does not react with 2-phenylpropionitrile in 50% aqueous NaOH, but the addition of a catalytic quantity of TEBA chloride immediately produces an exothermic reaction with the yield *ca.* 80% of the substitution product.

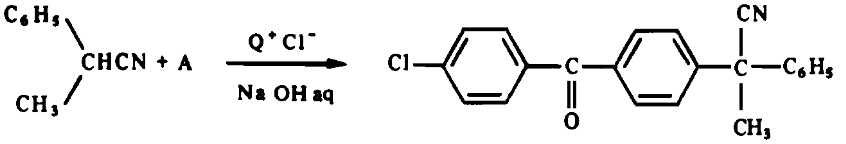
A model depicting a variety of reactions is 4-chloro-4-nitrobenzophenon (X). It contains four possible positions of attack:



X

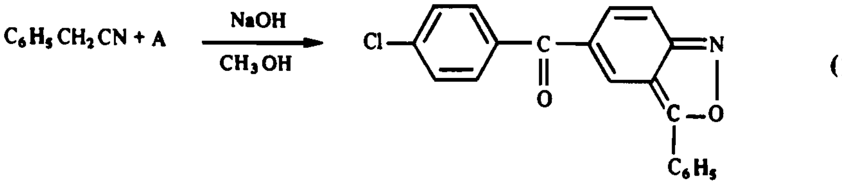
All these positions can be attacked by a suitable nucleophile, as can be seen in schemes (9–12) [69–71].

1. Substitution of the nitro group



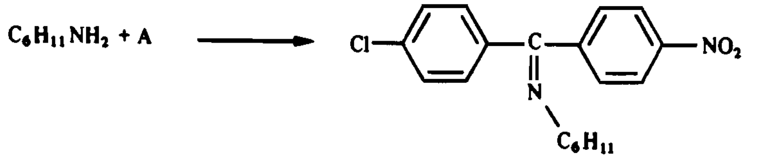
(9)

2. Substitution in position 2



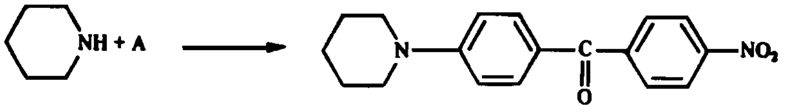
(10)

3. Attack of the carbonyl group



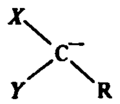
(11)

4. Substitution of chlorine



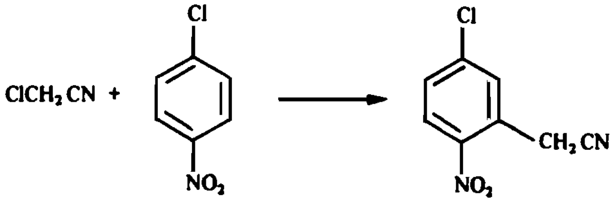
(12)

Another kind of substitution of nitro compounds was 'vicarious' substitution [72, 73], which takes place when the attack is carried out by a nucleophile



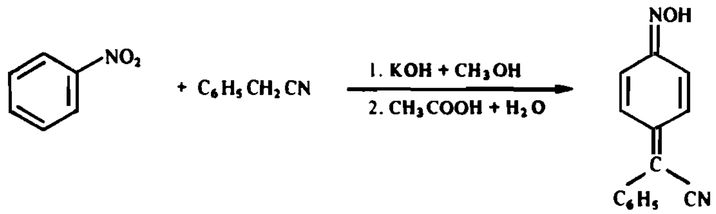
where *X* is a leaving group in a form of anion
Y is a group stabilizing carbanion

An example of such a substitution is reaction (13):



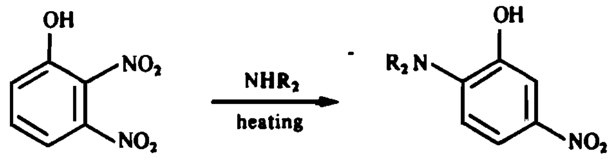
(13)

An example of nucleophilic substitution combined with a partial reduction of the nitro group was given by Davis and co-workers [74–76]. They examined the action of phenylacetonitryl anion on nitrobenzene and found that it formed a substitution compound with a *p*-quinoid ring according to scheme (14):



(14)

Cine-nucleophilic substitution is an interesting example of nucleophilic substitution with the loss of a nitro group. This was reviewed [77] and a few new examples were given: by Barnett, Dickens and West [78] and by Markwell [79]. The latter work gives an example of such substitution (15):



(15)

A nucleophilic introduction of an amino group into *p*-nitrobenzenephenone through the action of potassium amide in liquid ammonia was recently reported [80]. The substitution occurred in the *ortho* position to the nitro group with a yield of 17%.

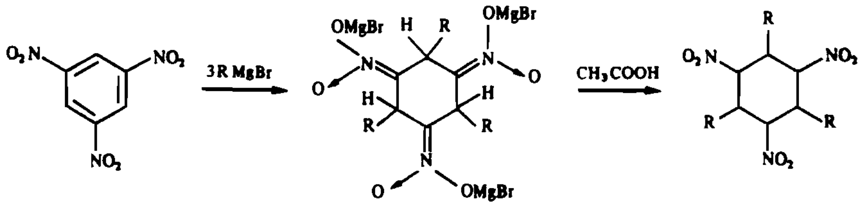
Important for industry is the reaction of the substitution of a nitro group by a sulphonic group as was described in Vol. I (pp. 201, 207). The mechanism of the reaction is now given in the chapter dedicated to the manufacture of TNT and other higher nitrated aromatics.

Salts of TNT (and strictly speaking salts of the products of decomposition of TNT through the action of strong bases) were described in Vol. I, pp. 303–304. They possess interesting pyrotechnic properties such as ease of burning. They seem to be the base of delay compositions described in a patent by du Pont de Nemours [220].

ACTION OF GRIGNARD REAGENT ON NITRO COMPOUNDS
(Vol. I, p. 186)

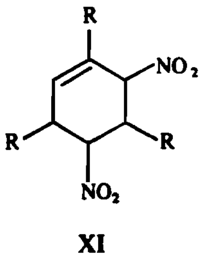
In addition to a few rather confusing papers on the action of Grignard reagent on nitro compounds (see 15), two papers should be mentioned: on the reduction of the nitro group to an amino group [81] and advice on how to carry out the reaction at low temperature (e.g. −70°C) otherwise undefined resinous products can be formed [82].

As it was stated, Severin (Vol. I, p. 187) obtained, 1,3,5-trialkyl-2,4,6-trinitrocyclohexane from 1,3,5-trinitrobenzene and Grignard reagent followed by acidification with acetic acid of the originally formed σ-complex, Severin and R. Schmitz [83] described fully the reaction as below (16):



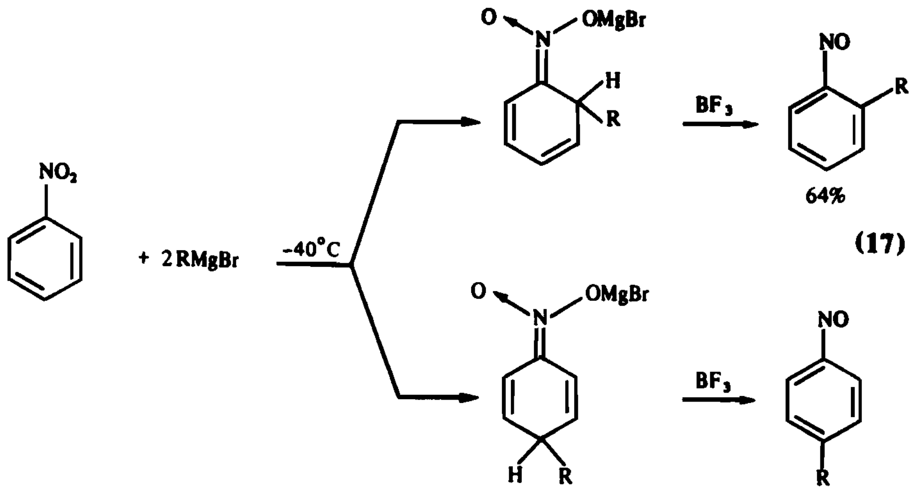
(16)

Similarly *m*-dinitrobenzene yielded a cyclohexene derivative (XI) [84]



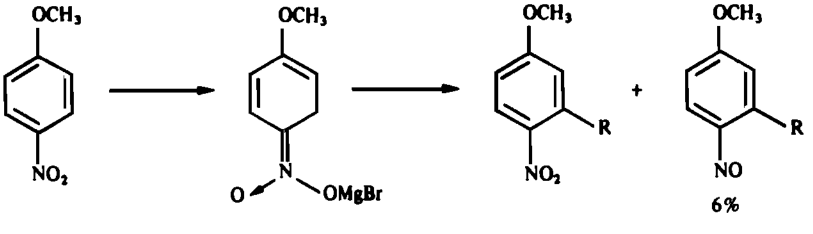
XI

Recently Bartoli and co-workers [85–87] have published a number of papers dedicated to the systematic study of the reaction of aromatic nitro compounds with Grignard reagent. They confirmed the nucleophilic character of the alkylation of the ring. They also found that under their experimental conditions the nitro group was reduced to the nitroso group (17):



(17)

However *p*-nitroanisol gave an 'anomalous' reaction (in the findings of Bartoli *et al.*). The main product was 3-alkyl-4-nitroanisol and only a small quantity of nitroso compound was found (18):



(18)

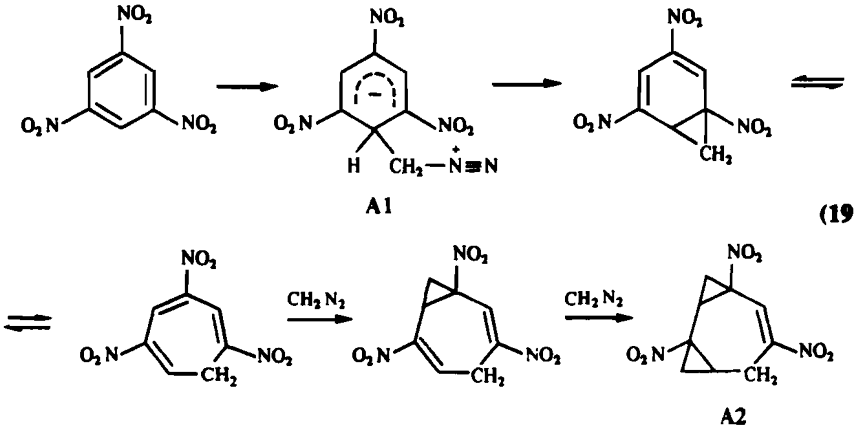
Bartoli and co-workers pointed out that their results did not contradict those of Severin and the differences were due to the different substrates and different experimental conditions.

Interesting cases of reactions of metal salts of secondary amines with nitrobenzene have also been recorded. Thus Montmollin [142] reacted potassium salt of carbazol with nitrobenzene. The nucleophilic substitution of nitrobenzene occurred in *para* position to the nitro groups. A similar reaction with diphenylamine [143] has also been described.

REACTION OF AROMATIC NITRO COMPOUNDS WITH DIAZOMETHANE (Vol. I, p. 195)

The reaction of 1,3,5-trinitrobenzene with diazomethane was carried out as early as 1898–1900 [88, 89], but only recently de Boer rationalized it as a nucleophilic addition leading to seven member ring condensed with two cyclopropane rings when the molar ratio of trinitrobenzene to diazomethane was 1:3. The first step of the reaction was a type of Jackson–Meisenheimer complex (A_1) and the final product was trismethylene-trinitrobenzene (A_2) [90–92a] (19). The reaction is temperature dependent: at −80°C compound (A_3) was formed.

With an excess of diazomethane (molar ratio 1:4) the last double bond can enter the reaction forming a stable pyrazoline ring not a cyclopropane (20)



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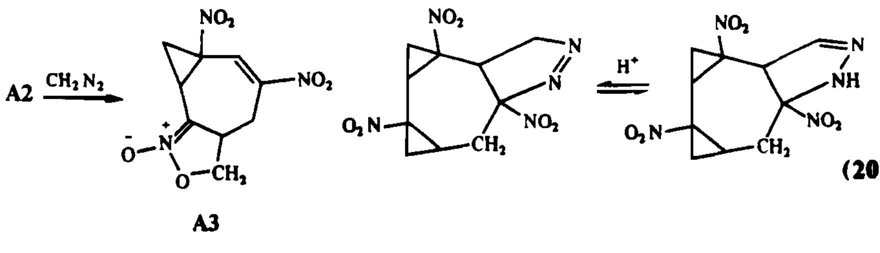
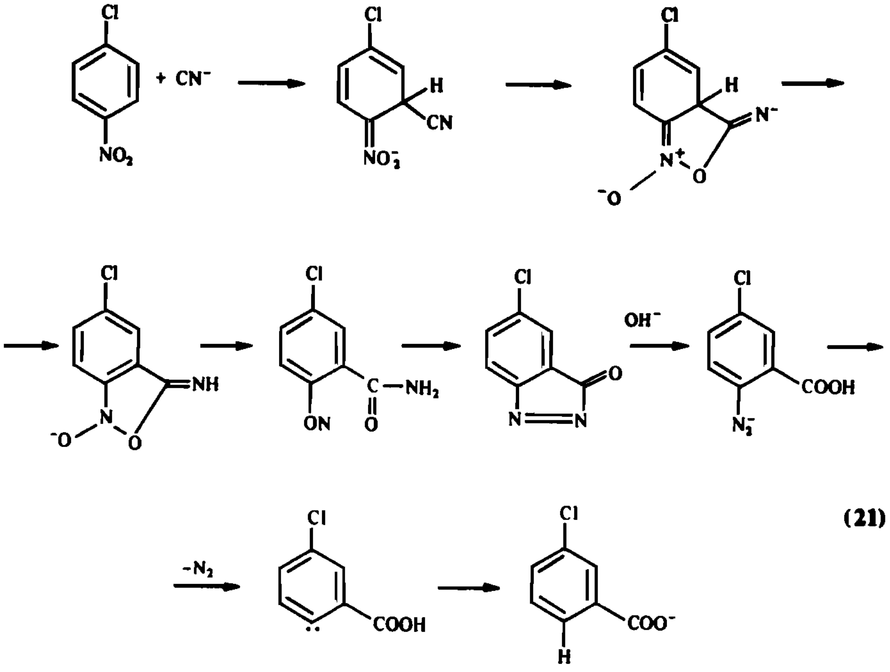


(20)

A similar reaction was given by picric acid which in the first instance was methylated to trinitroanizol [93].

MECHANISM OF RICHTER REACTION (Vol. I, p. 205)

In Richter reaction *m*-bromobenzoic acid may be obtained by reacting potassium cyanide with *p*-nitrobromobenzene. The original mechanism of the reaction given by Bunnett (Vol. I, p. 205) was further developed and can be presented in the form of scheme (21) [94, 95].



(21)

NUCLEOPHILIC SUBSTITUTIONS IN GAS PHASE

Nucleophilic substitutions can be carried out in gas-phase. Such reactions are much faster than in solution. They were recently reviewed by Bowie [47]. Some of these reactions are produced by radical anions.

REACTIONS OF RADICAL IONS

The reactions of radical ions form an important part of organic chemistry and a monograph [96] and review articles [97–101] have appeared.

A radical ion is a molecule which in addition to one or more unpaired electrons has a positive and negative charge in radical cation and anion respectively.

A formal presentation is shown in diagrams (22) according to [100]:

$$\begin{array}{ll} M + e \longrightarrow M^{\overset{-}{\cdot}} \text{ radical anion} & (a) \\ M - e \longrightarrow M^{\overset{+}{\cdot}} \text{ radical cation} & (b) \end{array} \qquad (22)$$

Radical anions of nitro compounds

The radical anions of nitrobenzene and substituted nitrobenzenes may be formed by electrolytic or metal reduction [100].

The treatment of *o*- and *p*-nitrotoluenes with a basic agent (e.g. potassium *t*-butoxide) in the absence of air can give rise to oxidation of nitrobenzyl radical anions which further react to yield dinitrodibenzyl [102]. The reaction can proceed through a radical chain mechanism [103] (23):

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \overset{\text{B}^-}{\rightleftharpoons} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \qquad \text{(a)}$$

$$p\text{-NO}_2\text{C}_6\text{H}_4^- + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3]^{\overline{\cdot}} + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^{\cdot} \qquad \text{(b)} \quad (23)$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^{\cdot} + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]^{\overline{\cdot}} \qquad \text{(c)}$$

Russell and co-workers [104] also examined the action of potassium *t*-butoxide on *p*-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, *m*-dinitrobenzene and 1,2,5-trinitrobenzene. The higher the nitrated hydrocarbons the slower the oxidation.

Hass and Bender [105] described a reaction of *p*-nitrobenzyl chloride with salts of nitroalcanes, for example of 2-nitropropane. The mechanism of the reaction was rationalized by Kornblum and co-workers [106] and Russell and Danen [107] as a sequence of chain reactions:

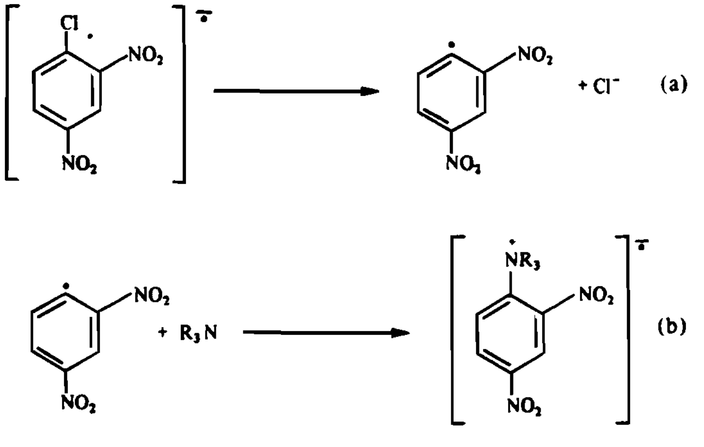
$$p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl} + (\text{CH}_3)_2\text{C}=\text{NO}_2^- \longrightarrow (\text{CH}_3)_2\dot{\text{C}}\text{NO}_2 + [p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl}]^{\overline{\cdot}} \qquad \text{(a)}$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl}]^{\overline{\cdot}} \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^{\cdot} + \text{Cl}^- \qquad \text{(b)}$$

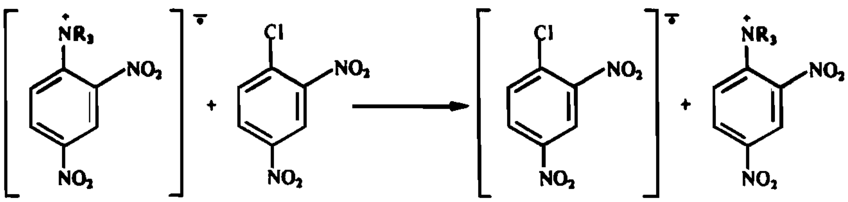
$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^{\cdot} + (\text{CH}_3)_2\text{C}=\text{NO}_2^- \longrightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2]^{\overline{\cdot}} \qquad \text{(c)} \quad (24)$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2]^{\overline{\cdot}} + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} \longrightarrow$$
$$\longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_2\text{NO}_2 + [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}]^{\overline{\cdot}}. \qquad \text{(d)}$$

Another example of chain reactions with radical anions was described by Shein and co-workers [108]: that is the reaction (25) between 2,4-dinitrochlorobenzene and trialkylamines:



(25)



(c)
(25)

An interesting example of a radical anion reaction is the action of oxygen negative ion formed in chemical ionization in a mass spectrometer [109]:

$$p\text{-}NO_2C_6H_4Cl + O_2^{-} \longrightarrow p\text{-}NO_2C_6H_4O^{-} + ClO. \qquad (26)$$

Nitroaromatics can act as catalysts of some oxidation reactions, such as the oxidation of benzoin [110] and polynitroaromatics in the oxidation of 'hindered' phenols [111]. Russell and co-workers [112a, b] rationalized it in terms of radical ion reactions where the radical ion Ar $NO_2^{-\cdot}$ activates oxygen (27):

$$Ar\,NO_2^{-\cdot} + O_2 \longrightarrow Ar\,NO_2 + O_2^{-\cdot}. \qquad (27)$$

FREE RADICAL REACTIONS (Vol. 1, p. 212)

A few monographs have been dedicated to free radical reactions including substitutions. The most important are those by Williams [113] and Sosnovsky [114] and a review article has appeared concerning the homolytic substitution of nitro compounds [115].

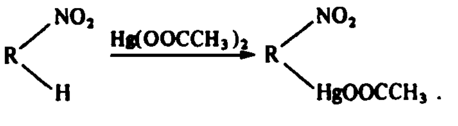
The nitro group activates aromatic rings towards a homolytic substitution. As previously pointed out the nitro group directs a substitution into *ortho* and *para* positions through the greater availability of an unpaired electron at the *ortho* and *para* positions and a greater stability of *ortho* and *para* quinoid which can be regarded as intermediates of some homolytic substitutions.

Some of the main reactions of aromatic nitro compounds with free radicals are given here [116]. Nitrobenzene reacts with hydroxyl produced by hydrogen peroxide ferrous salt reaction (28)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{-} + HO^{\cdot}. \qquad (28)$$

The reaction furnished *o*-, *m*- and *p*-nitrophenols with yields of 25–30%, 20–25% and 50–55% respectively.

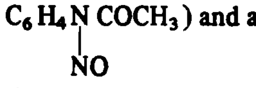
Another typical free radical reaction is that of mercuration of nitrobenzene with mercuric acetate in a non-polar solvent [117] (29):



$$R\begin{matrix}NO_2\\H\end{matrix} \xrightarrow{Hg(OOCCH_3)_2} R\begin{matrix}NO_2\\HgOOCCH_3\end{matrix}. \qquad (29)$$

Ortho and *para* isomers are formed in proportion in 57%, and *meta* in 43%. A relatively large proportion of *meta* isomer is probably due to the lack of a clear demarcation line between the electrophilic and the radical substitution.

A partial radical substitution may be responsible for the nitration of nitrobenzene to dinitrobenzenes by nitric acid in the presence of mercuric oxide reported by Ogata and Tsuchida [118]. They found 26% of *o*- and only 24% *m*-dinitrobenzenes.

Hey and co-workers [119–124] studied the arylation of nitrobenzene through the action of various sources of aryl radicals p-R $C_6H_4^{\bullet}$ generated from such sources as diazotates (p-R$C_6H_4N_2ONa$), nitrosoacylarylamines (p-R  $C_6H_4\underset{\overset{|}{NO}}{N}COCH_3$) and acyl peroxides ($p$-R $C_6H_4CO_2)_2$. The average substitution in the *meta* position for R = Br and CH_3 was only 12.1 and 8.6% respectively and was independent of the source of aryl radical.

The phenylation of nitrobenzene gave the figures shown in Table 25.

TABLE 25. Substitution of nitrobenzene with phenyl radical (average figures)

Source of phenyl radical	Nitrophenyls % *ortho*	 *meta*	 *para*
Sodium benzenediazotate	54	9	37
Benzoil peroxide	59.5	8.5	32

However, when the free radical is *p*-nitrophenyl, the proportion of *meta* isomer increases. This is explained by the fact that the radical p-$NO_2C_6H_4^{\bullet}$ is somewhat electrophilic in character.

Hey and Grieve [125] found in 1934 that the nitro group activates the aromatic ring towards homolytic substitution. For example, the competitive phenylation of toluene and nitrobenzene by phenyl radicals showed that the yield of nitrodiphenyls was about four times greater than the yield of methyldiphenyls.

Hey and co-workers [119, 121, 124] gave a quantitative analysis of the rate of homolytic attack on nitrobenzene as compared with that on chlorobenzene. The phenylation of nitrobenzene gave proportions of *ortho*, *meta* and *para* products: 58, 10 and 32% respectively, whereas the phenylation of chlorobenzene yielded 62, 24 and 14% respectively. However when the entering group is more electrophilic than benzene (e.g. *o*- and *p*-nitrophenyl radicals) the proportion of *meta* substituents increased.

Fields and Meyerson [127] have described in numerous papers the formation of free radicals from aromatic nitro compounds at temperatures of 400–600°C. Their work has been summarized in a review paper [128]. They found that the C — N bond in nitroaromatics breaks above 400°C generating phenyl and similar aromatic radicals. The decomposition at 600°C seems to be closely paralleled to its decomposition under electron impact in a mass spectrometer. Nitrobenzene at 600°C, gave within 20 s. a 30% yield of phenol, biphenyl, dibenzofurane, benzene, hydroxybiphenyl, nitrobiphenyl and in some instances of naphthalene.

In the presence of benzene, toluene, pyridine and tiophene, considerable proportions of biphenyl and terphenyl and their homologues and analogues were formed.

The mechanism of the reactions is rationalized by the authors, as follows (30):

$$\begin{tikzcd}
C_6H_5NO_2 \arrow[r, "\text{fast}"] \arrow[d, "\text{slower}"] & C_6H_5^{\bullet} + NO_2 \\
C_6H_5ONO \arrow[r] & C_6H_5O^{\bullet} + NO \arrow[d, "{[H]}"] \\
 & C_6H_5OH \\
C_6H_5^{\bullet} \arrow[r] & \text{biphenyl and terphenyl.}
\end{tikzcd} \qquad (30)$$

Naphthalene can be formed, according to the authors, through the intermediate formation of benzyne.

A few more free radical reactions of nitro compounds should be mentioned. Some of these reactions are photo-induced and are described in the chapter on photochemistry of nitro compounds.

In 1866 Kekulé [129] described the reaction of nitrobenzene with bromine at 250°C which under pressure yielded tetra- and hexabromobenzene [130], thus the replacement of the nitro group by bromine occurred. Later it was found [131] that chlorobenzene was the main product when acting with chlorine on nitrobenzene at 375°C in 46 s contact time with only a small proportion of chloronitrobenzenes. The substitution of nitro groups in *m*-dinitrobenzene by chlorine in gas phase at 200–300°C appears to be a commercial method of manufacturing *m*-dichlorobenzene [132]. Ponomarenko [133] studied this reaction and found the yield to be 92%. He also stated that aromatic nitro compounds are transformed into chloro derivatives by acting on nitro compounds with carbon tetrachloride at 220–310°C under pressure.

A similar, but probably nucleophilic substitution was studied by Lobry de Bruin and van Leent [134]. By acting with hydrochloride at 250°C they replaced nitro groups in dinitrobenzenes and *s*-trinitrobenzene to obtain dichlorobenzenes and *s*-trichlorobenzene respectively.

Gerstman and Bickel [111] observed that polynitroaromatics can act as catalysts in the oxidation of hindered phenols.

The mechanism of the catalytic action of aromatic nitro compounds was not clear until Russell and co-workers [136] rationalized it in terms of free radical reactions. Their particular study was dedicated to the oxidation of fluorene by molecular oxygen in ter-butoxide in the presence of potassium ter-butoxide. The reaction is catalysed by aromatic nitro compounds, such as nitrobenzene and particularly *m*- and *p*-dinitrobenzene and *p*-bromo- and *p*-chloronitrobenzene.

A rather unusual free radical reaction should be mentioned here: aryl free radical produced by heat or copper powder can displace and substitute a nitro group [172, 173].

ACTION OF AROMATIC NITRO COMPOUNDS ON POLYMERIZATION

(Vol. I, p. 214)

Aromatic nitro compounds inhibit radical polymerization. However, they do not seem to inhibit ionic polymerization [137]. On the contrary Rumanian authors reported [190] that nitrobenzene as well as nitromethane and nitroethane increase the rate of cationic polymerization of *N*-vinylcarbinol.

With regard to radical polymerization some controversial results have also been obtained. Thus Mondvai and co-workers [138] have shown that *o*-dinitrobenzene was a stronger retardant of radical polymerization of methyl methacrylate than other isomers. On the contrary Hammond and Bartlett [139] found that *o*-dinitrobenzene was a weaker retardant than other isomers of polymerization of allyl acetate.

T. Urbański and Buźniak [140, 141] undertook the task of a systematic study of the action of mono-, di- and trinitro derivatives of benzene and toluene (a few dozen compounds) on the polymerization of unsaturated polyester resin 'Polymal 109'. The polymerization was initiated with benzoil peroxide at 12°C. It was found that nitro compounds with an *ortho* substituent are particularly active as inhibitors of polymerization.

The strongest inhibitor was found to be *o*-nitrotoluene.

Steric factors, such as those produced by two methyl groups in *ortho* position reduces the inhibitory activity of the nitro compounds.

Tüdös and co-workers [175] described inhibition of polymerization of styrene by *sym*-trinitrobenzene.

All these studies may have a certain significance in the technology of solid propellants for rockets. Szyc-Lewańska and Syczewski [227] examined the inhibition of polymerization by nitro compound. A difference was noticed between the action of aromatic and aliphatic nitro compounds. The action of aliphatic nitro compounds is less pronounced. Nitrate esters of nitro alcohols accelerate visibly the polymerization of methyl methacrylate and styrene.

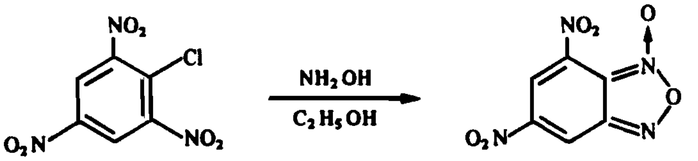
REDUCTION OF AROMATIC NITRO COMPOUNDS. FORMATION OF NITROSO COMPOUNDS

The reduction of the nitro group to amino and hydroxyamino groups is well known and described in textbooks dedicated to intermediates and dyestuffs.

Less known is the reduction of nitro to nitroso group. It was reviewed by Boyer in a chapter 'Reduction and Deoxygenation of Nitro Compounds' [147]. The following are methods giving good yields of nitroso derivatives:

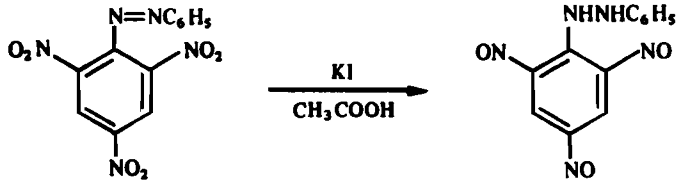
electrolytic reduction [148],
catalytic reduction in the presence of iron powder in CO_2 at 220°C [149],
deoxygenation of nitro group by free radicals [150].

Reduction of a nitro group can lead to a ring closure to form furoxane derivatives [151]



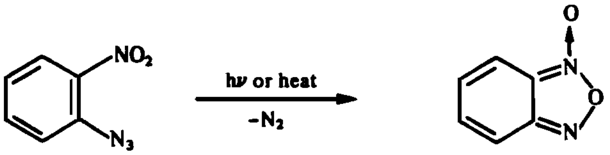
(31)

Another interesting reaction was reported by Willgerodt [152] on the action of potassium iodide in acetic acid on *N*-1,3,5-trinitrosophenyl-*N*-phenylhydrazine (from picrylazobenzene) (32):



(32)

The classical photochemical reaction of Ciamician and Silber [153] of *o*-nitrobenzaldehyde transformed into *o*-nitrosobenzoic acid is described in the chapter on photochemistry of nitro compounds. *o*-Nitrophenyl azide can readily yield benzofuroxane [154].



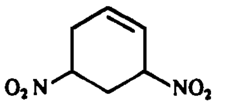
(33)

It is highly probable that a nitroso intermediate is formed in the Richter reaction (p. 109).

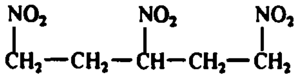
Reduction of Aromatic Ring

A remarkable reaction was discovered by Severin and co-workers [155, 156] (Vol. I, p. 252). He succeeded in reducing the aromatic ring of nitro compounds without reducing the nitro groups. The reducing agent was sodium borohydride. *s*-Trinitrobenzene was dissolved in tetrahydrofurane and $NaBH_4$ in aqueous methanol was added at 0°C. 1,3,5-Trinitrocyclohexane resulted in a yield of 40% [155]. 1,8-Dinitronaphthalene was reduced by the same method to 1,4-dihydro-1,8-dinitronaphthalene (78% yield).

m-Dinitrobenzene was partially reduced [156] to 3,5-dinitrocyclohexene (XI) and picric acid to 1,3,5-trinitropentane (XII) through the ring opening.



XI



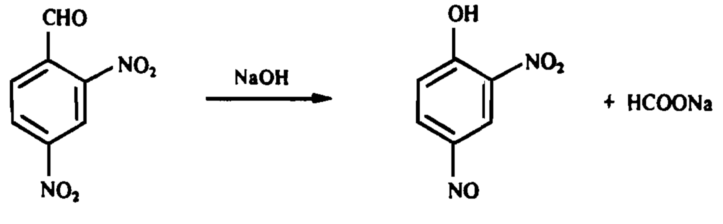
$$\overset{NO_2}{CH_2}-CH_2-\overset{NO_2}{CH}-CH_2-\overset{NO_2}{CH_2}$$

XII

The reaction has been studied by a number of authors [157, 158], who came to the conclusion that the hydride reacts initially on the electron-deficient carbon atom at position 3 and forms a kind of Jackson–Meisenheimer adduct, the latter is eventually subject to reduction.

Okamoto and Attarwala [159] brought an improvement to the reaction of Severin, by adding a cationic surfactant (as a phase transfer catalyst) to the reaction medium. They examined the reduction of unsymmetrically substituted -2,4,5- and 2,3,4-trinitrotoluenes by sodium borohydride in methylene dichloride at 23–24°C in the atmosphere of nitrogen in the presence of ethylhexadecyldimethylammonium bromide.

An interesting instance of oxido-reduction of a nitro compound was given by Forbes and Gregory [180]. 2,4-Dinitrobenzaldehyde when warmed with a concentrated solution of sodium hydroxide yielded 2-nitro-4-nitroso instead of the expected acid and alcohol according to the Cannizzaro reaction.



(34)

The reaction is similar to that of Ciamician and Silber – a classical photochemical reaction (Chapter V).

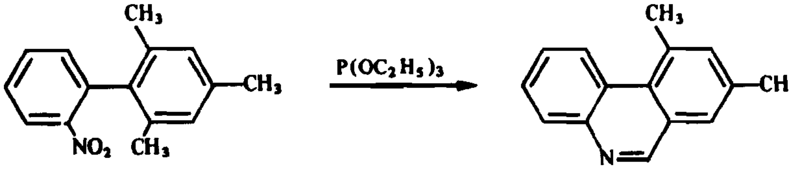
A partial reduction of the aromatic ring of trinitrobenzene was recently described by Ohno, Yamamoto and Oka [160]. By acting with 1,4-dihydronicotinic acid derivatives, 1,3,5-trinitrobenzene was reduced to dihydrotrinitrobenzene at room temperature in dry acetonitryl in the atmosphere of argon and away from light.

Sodium amide can reduce the nitro group of aromatic nitro compounds to give a small yield of diazo compounds [161, 162].

Kemula and co-workers [163] developed the polarographic reduction of the nitro group as an analytical method.

The case of the reduction of nitro compounds leads to their use as oxidizing agents. The use of nitrobenzene in the Skraup reaction is well known. *o*-Dinitrobenzene was reported to be a good agent for oxidizing ascorbic acid to diketone [164].

A nitro group can yield *N*-heterocycles (see Vol. 1, p. 195) through the action of various reducing agents such as metal oxalates [165, 166], triethyl phosphite [167–169] or iron pentacarbonyl [170] (35):



(35)

The reaction of nitro aromatic compounds with carbon monoxide was recently reviewed by Manov-Yuvenskii and Nefedov [221]. Particularly interesting is the formation of isocyanates apparently produced in the same way in Japan [222].

DIAZOTIZATION OF AMINO NITRO COMPOUNDS

The NO$_2$ group reduces the basicity of amino group and makes the diazotization more difficult. Diazotization of dinitro aniline and particularly trinitroaniline requires more drastic conditions, such as the use of more concentrated acid medium and higher temperature. This can be found in textbooks on diazotization and on dyestuffs chemistry.

On the other hand the nitro group renders the diazo group more electrophilic and more reactive in the process of coupling to form azo compounds. Thus 2,4,6-trinitrobenzodiazonium ion couples with mesitylene which is less reactive than anisole and does not react with other diazonium ions [171].

Reactions of the replacement by hydrogen of the tertiary nitro group in aliphatic and alicyclic compounds were recently described by Kornblum and co-workers [145]. They occur at room temperature when the nitro compounds are treated with the sodium salt of methyl mercaptan.

Łytko-Krasuska, Piotrowska and T. Urbański [146] described the replacement by hydrogen of tertiary nitro group in 5-nitro-1,3-dioxane by acting with ethylene glycol in KOH at 120–140°C with yields of up to 60%.

An interesting case of the substitution of nitro group by adamantyl radical was reported by Italian authors [188]. Free adamantyl radical was produced from carboxylic acid according to [187].

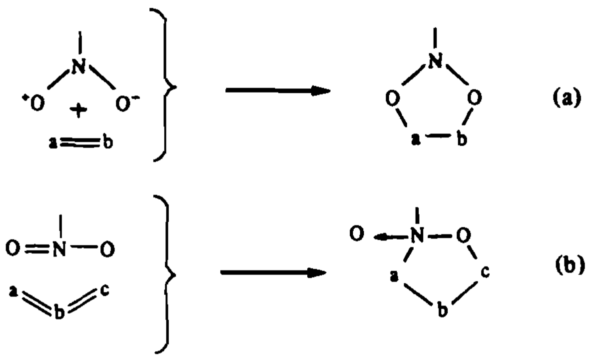
1,3-CYCLOADDITION OF NITRO COMPOUNDS

Nitro compounds can be subjected to the so-called 1,3-cycloaddition which is manifested by adding a system with double bonds to 1,3-dipole.

1,3-Dipole can be represented in two limiting forms: a sextet and an octet:

$$\underset{\text{sextet}}{{}^{+}O—N—O^{-}} \qquad \underset{\text{octet}}{O=N^{+}—O^{-}}$$

Cycloaddition can be represented by schemes (36): (a) and (b)

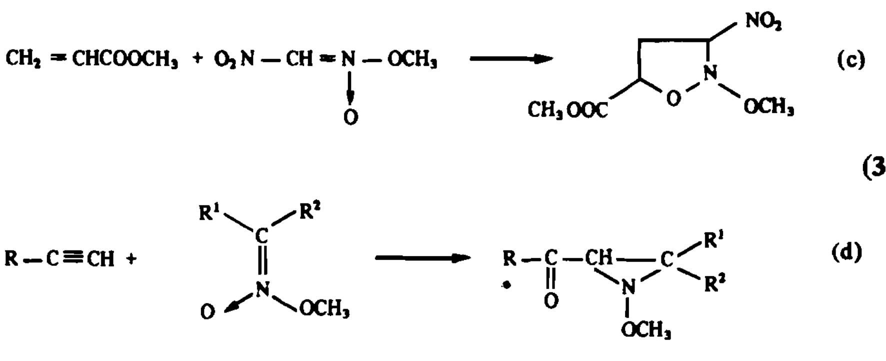


(36)

An excellent review of 1,3-cycloaddition was given by Huisgen [135].

A considerable number of experiments with 1,3-cycloaddition were reported by Tartakovskii, Novikov and co-workers [181–185]. They reacted nitronic acid esters (esters of aciform of primary or secondary nitro alkanes) with dipolephiles such as styrene, vinyl chloride, acrylic esters and methyl–vinyl ketone (36c). The reaction occurs at room temperature (or lower) with an excess of unsatured compound, the yield is 60–90%.

The reaction of nitronic acid esters with acetylene derivatives yielded aziridines (36d) [186].



(36)

Some 1,3-cycloadditions occur under irradiation with ultraviolet light. They are described in Chapter V (reactions by Büchi and Ayer and by Charlton and de Mayo).

THERMAL STABILITY OF AROMATIC NITRO COMPOUNDS

It is generally accepted that aromatic nitro compounds are thermally stable and are only sensitive to the action of bases which produce deep changes in their structure. Nevertheless the action of high temperature on TNT had already been examined in 1911–12 by Verola (Vol. I, p. 306). He found that an evolution of gases started when TNT was kept at 160°C, and the m.p. of TNT was reduced from 80.75° to 79.9°C after keeping the substance for 177 hours at 145–150°C. Thus Pasman, Groothuizen and Vermeulen [191] made a statement that 'fused TNT is unstable at elevated temperatures (> 150°C)'.

The high thermal stability of nitro compounds is manifested by the high activation energy E of their thermal decomposition. The following are figures referring to mono-, di- and trinitro compounds:

Nitrobenzene $E = 53.4$ kcal/mol, log B = 12.65 at 395–445°C
m-Dinitrobenzene 52.6 kcal/mol, log B = 12.7 at 345–410°C
1,3,5-Trinitrobenzene 51.9 kcal/mol, log B = 13.6 at 270–355°C

as given by Maksimov [192].

Andreev [193] gave figures for:

$$\left.\begin{array}{l}\text{Picric acid,}\quad E = 38.6\ \text{kcal/mol, log B} = 11.6\\ \text{Styphnic acid,}\ E = 34.6\ \text{kcal/mol, log B} = 11.2\end{array}\right\}\ \text{at } 183\text{–}270^\circ\text{C.}$$

Roginskii and Magid [194] found $E = 27.0$ kcal/mol and log B = 11.4 for the decomposition of TNT.

Similar figures were obtained by Robertson [195], Pasman *et al.* [191] for the temperatures in the interval of 126–196°C, and for higher temperatures (380–440°C) T. Urbański [196] found 14.0 kcal/mol.

Pasman *et al.* [191] carried out experiments on thermal decomposition of TNT using the adiabatic storage test method. They found that the total heat evolved during 120 hours of keeping at 175°C was 74 kcal/kg.

A few accidents which have recently occurred demonstrate that prolonged heating, much below their ignition temperature, (the deflagration point) can produce an explosion even if this is referred to lower nitrated compounds. Such an accident was recorded (probably for the first time) in 1972 when an explosion took place at 218°C in the U.S.A. in a 100 m long pipe filled with dinitrotoluene [197]. Previous experiments determined ignition temperature as being 270°C, although some sources give an even higher temperature of 300°C [198]. The problem revived in 1976 in the United Kingdom when 1300 kg of 3,5-dinitro-*o*-toluenediamine kept in a closed drier at 118–130°C exploded after 27 hours of heating [199]. In order to create a method which could be used to establish the stability of aromatic and possibly other nitro compounds, Camera and Biasutti [199] developed an ingenious method of 'Isothermal Pressure Meter' which is a perfection of the method used by Small and co-workers. The method consists in keeping a sample 65 g in a steel pressure vessel in a thermostat (accuracy ± 0.2°C). The induction period is considered to be terminated when the pressure in the vessel increased by 0.2 kG/cm^2. The experiment was continued until the disc closing the vessel was ruptured.

For DNT (a mixture of 2,4- and 2,6-dinitrotoluene) the induction period was found to be:

175000 hours at 100°C
1040 hours at 150°C
18 hours at 200°C

The calculated energy of activation was 32.2 kcal/mol.

The addition of 2,4,6-trinitrotoluene to DNT reduced the induction time at 235°C, viz.:

pure DNT	1.70 hours
TNT:	1.70 hours
addition of 5000 ppm TNT	1.53 hours
25,000 ppm TNT	1.09–1.14 hours
50,000 ppm TNT	0.88–1.00 hours
100,000 ppm TNT	0.20

Similar influence was shown by addition of 2,4-dinitro-*o*- and 2,6-dinitro-*p*-cresols.

Attention is also drawn to the paper by Dacons, Adolph and Kamlet [200] who described a spontaneous self-ignition of TNT after being kept for 14–16 hours at 210°C.

A review of kinetic data from low-temperature thermolysis of polynitro compounds was recently given by Zeman [201].

Free Radicals

In the course of thermal decomposition of aromatic nitro compounds free radicals are formed. The ESR signals were detected by Janzen [202], Japanese workers [203] and Soviet workers [204]. The latter authors obtained strong signals from picric acid after an induction period of 30–5 min at 190–210°C respectively.

Janzen reported the formation of free radicals in 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and picric acid at 260°, 240° and 130°C respectively. 2,4-Dinitro- and 2,4,6-trinitroaniline give the signal at room temperature. This can be rationalized by the author of the present book in terms of the intramolecular charge–transfer as described by T. Urbański *et al.* [205], that is when the molecule contains both electron donor and electron acceptor groups.

FUROXANES (Vol. I, p. 603)

Aromatic nitro compounds which in *ortho* position have azido group can readily be transformed into benzofuroxanes (31, 33). An excellent review on furoxanes was written by Kaufman and Picard [206]. Recent works on the structure of benzotrifuroxane were also published: on X-ray analysis [207, 208], vibrational and Raman spectra [209, 210], nitrogen NMR [211], carbon 13 NMR [212]. Explosive properties were also discussed [213].

Korsunskii and Apina [214] examined the kinetics of the transformation of 1,3,5-triazido-2,4,6-trinitrobenzene into benzotrisfuroxane at 70–115°C. The reaction is of the first order with activation energy 26 kcal/mol.

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CHAPTER 5

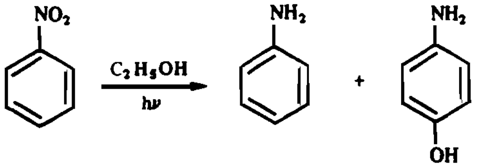
PHOTOCHEMISTRY OF NITRO COMPOUNDS

(Vol. I, p. 225)

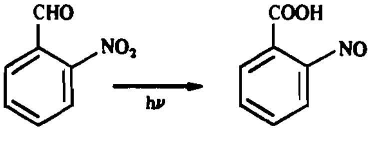
Photochemistry has received much appreciation in the last two decades manifested by several fine monographs and review articles. Most of them have a general character [1–5]. Excellent reviews dedicated to photochemistry of the nitro and nitroso groups were given by Morrison [6], Carless [35] and Kaye [47].

It is assumed that photochemical reactions originate from the lowest energy singlet and triplet excited states. They are due to absorption bands which have been described in Chapter III on the spectroscopy of nitro compounds: the $\pi \longrightarrow \pi^*$ transition (*ca.* 210 nm) of high intensity and $n \longrightarrow \pi^*$ (*ca.* 270 nm) of a relatively low intensity; some nitro compounds show the second transition $n \longrightarrow \pi^*$ (*ca.* 350 nm). It is accepted that the lowest lying singlet and triplet states for nitro compounds are n, π^*.

The photochemistry of nitro compounds began with the pioneering work of Ciamician and Silber [7, 8] who described two photochemical reactions (1, 2):



(1)



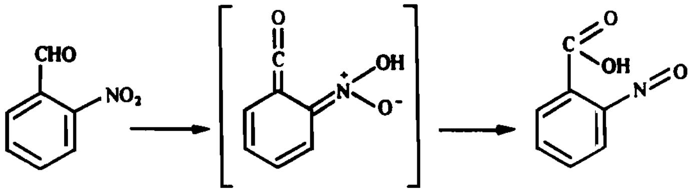
(2)

In reaction (1) ethanol is oxidized [9, 10] to acetaldehyde, nitrobenzene is reduced partly to phenylhydroxylamine (which rearranges into *p*-aminophenol) and partly to aniline.

Reaction (2) in alcoholic medium was examined by Bamberger and Elger

[11], who found that it passed through the formation of acetals.

Recently George and Scaiano [12] examined the reaction of Ciamician and Silber and came to the conclusion that photolysis of *o*-nitrobenzaldehyde proceeded by a triplet state with a life-time of 0.6 ns. Laser flash photolysis showed the formation of a transient intermediate according to (3):

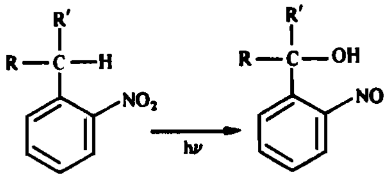


(3)

Similar photochemical reactions were recorded for 2,4-dinitrobenzaldehyde [13] and nitroterephthaldehyde [14].

o-Nitrobenzyl ester yielded *o*-nitroso benzaldehyde [48a] by the same mechanism.

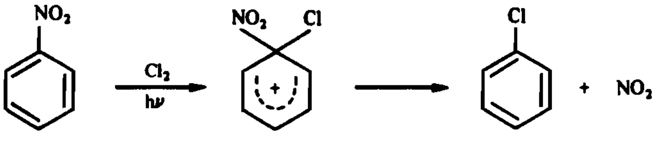
A rule of Sachs and Hilpert [15] should be mentioned: "all aromatics which have a hydrogen *ortho* to a nitro group are light sensitive". They expressed it by a scheme (4)



(4)

Photolysis of nitramine derivatives of steroids has also been recently described [16].

Some photoinduced reactions of nitro compounds involving a formation of free radicals or radical ions were reviewed by Traynham [17]. He classified such reactions as occurring through the "*ipso*" attack, that is, the entering group is (in the first instance) attached to the same carbon as the group to be removed, as in the classical case of replacing the nitro group of nitrobenzene by chlorine under the action of light:

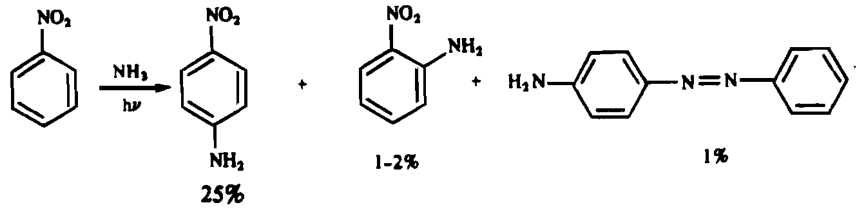


(5)

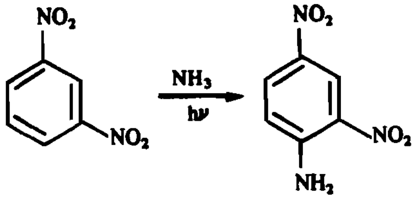
(see also [18] and [19]).

Some reactions described in [6] merit particular attention, for example:

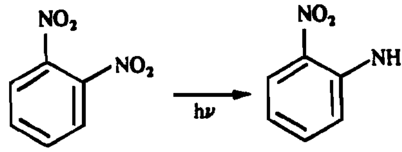
Havinga, de Jongh and Dorst [20] reported the photoinduced hydrolysis of *m*-nitro phosphoric ester to *m*-nitrophenol. *m*-Nitroanisol was also hydrolysed to *m*-nitrophenol [21] and by the action of potassium cyanide yielded *m*-cyanonitrobenzene [22]. Gold and Rochester [23] reported the formation of 3,5-dinitrophenoxide ion from *s*-trinitrobenzene and hydroxylic ion. Van Vliet [24] obtained a number of nitro derivatives of aniline by acting with liquid ammonia on some aromatic nitro compounds under irradiation with ultraviolet-light, viz. (6), (7) and (8):



(6)



(7)



(8)

Photoinduced condensation of *m*-dinitrobenzene and *sym*-trinitrobenzene to nitro derivatives to azoxybenzene was reported by Stenberg and Holter [36]. The most important factor is the solvent. The reaction does not proceed in benzene but gives a good yield in tetrahydrofurane. In ethanol a smaller yield was obtained and ethanol was partly oxidized to acetaldehyde, as found in other reactions [9, 10].

A few papers by Reid and co-workers [37] and de Boer and co-workers [60, 61] were dedicated to the photochemistry of aliphatic nitro compounds. The photochemistry of 17-nitrosteroids was also described [38].

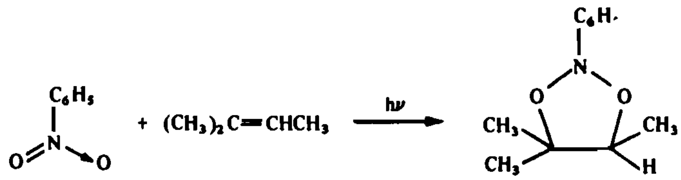
An interesting instance of remote oxidation with photoexcited nitrobenzene derivatives was given in [39].

An excellent review was given by Frolov, Kuznetsov and Eltsov [52] on the photoreduction of aromatic nitro compounds through intermolecular action. Alcohols and hydrochloric acid supply the hydrogen needed for reduction: alcohols are converted into aldehydes, as in reaction (1) and hydrochloric acid becomes a strong chlorinating agent, for example [53].

Gold and Rochester [54] and Johnson and Rees [55] described a transformation of 1,3,5-trinitrobenzene into 3,5-dinitrophenol under photochemical action of OH^- [compare with reaction (11) in Vol. I, p. 251].

Wan and Yates [56] reported the photochemical oxidation of *m*-nitrobenzyl alcohol in aqueous solution to *m*-nitrobenzaldehyde and azoxy compounds.

An interesting photochemical reaction of 1,3-cycloaddition (see Chapter IV) was reported by Büchi and Ayer [58] (9)



(9)

A similar reaction to the addition of nitrobenzene to cyclohexane was reported by Charlton and de Mayo [59].

A heterolytic substitution of 1-methoxy-3,5-dinitrobenzene through the action of ultraviolet light was described by Havinga and co-workers [57]. 3,5-Dinitrophenol resulted, i.e. demethylation occurred.

ALIPHATIC AND ALICYCLIC NITRO COMPOUNDS

A primary photochemical reaction of nitro alkanes is a cleavage of the C—N bond [47, 48]:

$$CH_3NO_2 \xrightarrow{h\nu} CH_3^{\cdot} + NO_2 \qquad (10)$$

followed by recombination to yield methyl nitrite

$$CH_3^{\cdot} + NO_2 \longrightarrow CH_3ONO. \qquad (11)$$

For a full discussion of the reactions see [6] Vol. I, p. 583 and Chapter VIII.

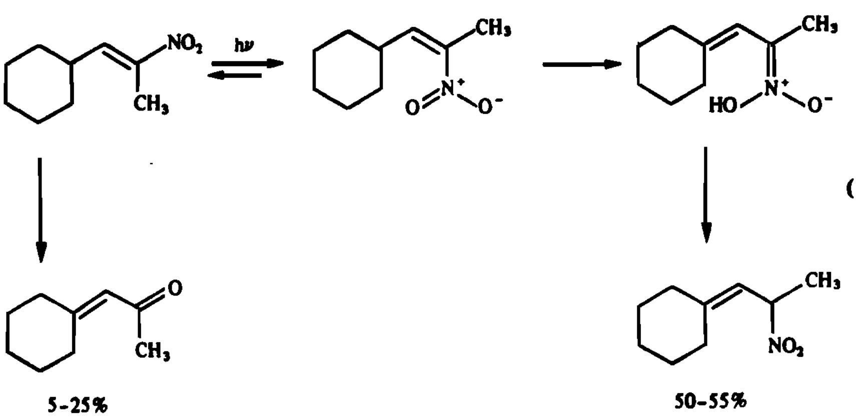
Photochemistry of nitromethane and its substituted derivatives (XCH_2NO_2, X = CH_3, NH_2, F, and F_2CHNO_2, F_3CNO_2) was examined by Slovetskii and co-workers [49]. They came to the conclusion that the transition from the ground state to the triplet state leads to an increase of the density of the positive charge at the central carbon atom and decrease at the nitrogen. They also suggested probable conformation of monosubstituted derivatives of nitromethane. Slovetskii *et al.* [50] also examined the photolysis of tetranitromethane:

$$C(NO_2)_4 \xrightarrow{h\nu} C(NO_2)_3^- + NO_2^+. \qquad (12)$$

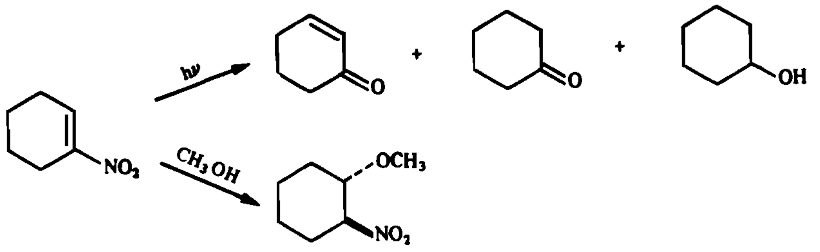
The reaction is influenced by solvents and begins by a triplet state.

An important reaction is the photochemical 1,2-cycloaddition of nitroalkenes [6].

S. T. Reid and co-workers [51] examined the photochemistry of some nitro alkenes. They are depicted by formulae (13) and (14):



(13)



(14)

Photoconductivity of Nitro Compounds

The phenomenon of photoconductivity, that of nitro compounds was recently reviewed by Jarosiewicz [25].

Photoconductivity of liquid nitrobenzene was described by Brière and Gaspard [26]. They rationalized it as the result of photoionization of the compound. The increase in conductivity occurred in the course of irradiation by the light of the wave-length corresponding to the absorption by nitrobenzene. The process is reversible when irradiation is of short duration, but after prolonged irradiation it can attain a constant value.

Some authors have drawn attention to the fact that photoconductivity can be due to impurities in nitrobenzene [27]. On the other hand it is known that radico-ions can be formed in pure nitrobenzene under the action of an electric current [28].

Szychliński [29] described the same phenomenon and found the influence of the solvent, for example the photoconductivity, is prominent in ethyl ether or

1,4-dioxane but less noticeable in benzene. This author explains it in terms of the formation of CT (EDA) complexes. An important finding was made by Japanese authors [30, 31] that 1,3,5-trinitrobenzene shows a strong photoconductivity. Among other aromatic nitro compounds 2,4,7-trinitro-9-fluorenone possesses similar properties [32].

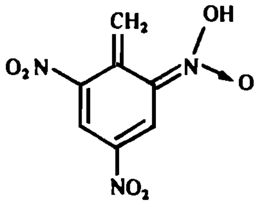
Also nitroalkanes have demonstrated photoconductivity [33, 34].

An interesting proof has recently been given of photochemical splitting of free radical NO_2 from nitroalkane: Marciniak and Paszyc [62] irradiated nitromethane dissolved in cyclohexane and received nitrosocyclohexane dimer:

$$CH_3NO_2 \xrightarrow[(254\text{ nm})]{h\nu} CH_3^{\bullet} + {\cdot}NO_2 \xrightarrow{\text{cyclohexane}} \text{trans-nitrosocyclohexane dimer}$$

PHOTOLYSIS

Flash photolysis of aromatic nitro compounds was carried out by a number of authors: Wettermark [40], Suryanarayanan, Capellos, Porter and co-workers [41–43]. Among various findings the latter authors came to the conclusion that 2,4,6-trinitrotoluene under flash photolysis is transformed into aci-quinoid isomer (I) with an absorption maximum at 460 nm.



I

Important contributions to the mechanism of photolysis of aliphatic nitro compounds were made by Bolsman, de Boer and co-workers. In the first paper Bolsman and de Boer [44] examined photolysis of 'pseudonitrole' 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen. This is described in Chapter VIII.

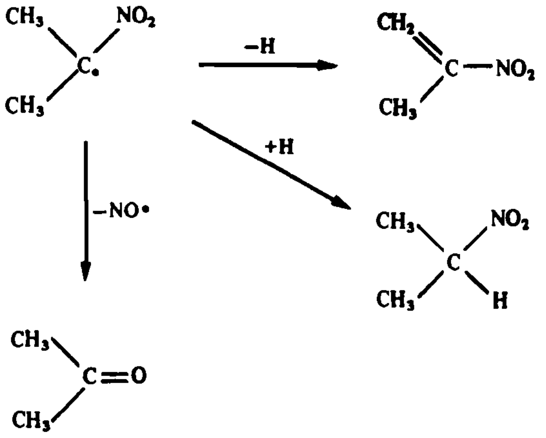
In further experiments Bolsman, de Boer and Verhoeven [45] examined the photochemical decomposition of 2-iodo-2-nitroadamantane in several hydrogen donating solvents and found the formation of α-nitroalkyl radical. This was extended to simple α-iodonitroalkanes in solution [46].

The formation of α-nitroalkyl radical can be depicted by reaction (15):

(15)

The evidence of the formation of the radicals was given by ESR signals.

Further reactions of a simple radical in inert solvents can be presented by scheme (16):



(16)

For more details on the photochemistry of nitro compounds see *Encyclopedia of Explosives* [47].

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CHAPTER 6

NITRO DERIVATIVES OF BENZENE
(Vol. I, p. 230),
TOLUENE (Vol. I, p. 265)
AND OTHER AROMATICS

The properties of higher nitrated derivatives of benzene and toluene were given in Vol. I (pp. 230, 265) and more detailed and modernised data in the monograph by Meyer [1]. Only those properties which have not been recorded in the said books or given in the literature recently will be mentioned here. With regard to the chemical properties, one of the most characteristic features of polynitro aromatics is their ability to nucleophilic substitution. This is discussed in Chapter IV in general terms and some features will be given here in the description of particular nitro compounds.

NITRATION OF BENZENE TO NITROBENZENE

The heterogeneous nitration of benzene has been reviewed by Albright, Hanson and co-workers [2]. They drew attention to the problem of diffusion control which has already been discussed in Chapter II. The differences between the results of various authors was partly due to insufficient appreciation of the problem of diffusion. It is true that nitration occurs mainly in the acid phase and at the interface between acid and organic phases. However, the role of diffusion and solubility of organic compounds in each phase can be decisive and so is adequate mixing. The authors also described their own work where they used a continuous flow stirred tank reactor of 50 ml capacity made of stainless steel and jacketed for temperature control. The agitator of 2.5 cm diameter was a four-blade operator at 3000 rpm. They found that the solubility of benzene in acids changed almost linearly as the concentration of nitric acid changed in the mixed acids. The solubility of benzene was about four times greater than that of toluene. Subsequently the nitration of benzene is only 5 times slower than the nitration of toluene, although earlier reports gave a figure of 20 times slower. The latter figure was based on one phase nitration systems and can be misleading for industrial reaction.

Nitrobenzene (Vol. I, p. 231)

Although it is not an explosive, nitrobenzene created an interest as an intermediate in the formation of di- and tri-nitrobenzene. Also it was known that at high temperature in the presence of an alkali it is subjected to explosive decomposition.

Powerful liquid explosives mixtures of nitrobenzene and liquid N_2O_4 were also known and in some use (Vol. III, p. 289). Recently pyrolysis of nitrobenzene was examined in the range of 275–630°C [3]. At lower temperatures nitrobenzene decomposes via direct rupture of the C–N bond to give free radicals $C_6H_5\cdot$ and $\cdot NO_2$. As the temperature was raised the yield of NO_2 considerably decreased and at 625°C the volatile products were composed of:

1.2%	NO_2
28.0%	NO
1.2%	N_2O
61%	CO
8%	CO_2

The liquid products contain: benzene (21%), phenol (19%), diphenyl (8%), benzonitrile (5%), dibenzofurane (8.5%), benzoquinoline (2.5%) among other less defined substances. Among earlier papers see also that of Fields and Meyerson [4] (see p. 113), Hand, Merrit and Di Pietro [5] which referred to phenyl free radical and nitrobenzene formed by pyrolysis.

Nucleophilic substitution of nitrobenzene with some carbanions was described in Chapter IV.

The industrial method for the nitration of benzene to nitrobenzene is described in the paragraph dedicated to nitration of toluene.

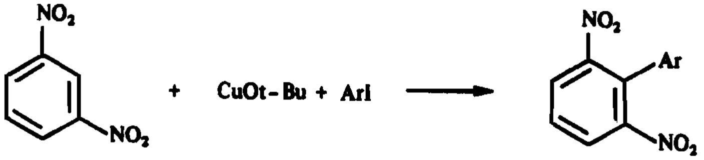
m-Dinitrobenzene

An early paper on the crystal structure of *m*-dinitrobenzene should be mentioned [6]. The method of Fourier series and a projection of the electron density gave the following result. Benzene ring is a regular hexagon of side 1.41 Å. C–N bonds do not lie in the plane of the ring but make an angle of 15° with it. The C–N distance is 1.54 Å, the N–O distance has been found to be 1.20 Å and O–O distance in the nitro groups is 2.17 Å.

An interesting synthesis of biaryl systems which is a modification of the Ullmann method was recently given by Cornforth and Wallace [7]. It consists in acting upon *m*-dinitrobenzene with aryl iodides under the influence of copper *t*-butoxide (1).

The yield of 2.6-dinitrodiphenyl derivatives varied from 10 to 96% depending on aryl.

New data have appeared on the vapour pressure of *m*-dinitrobenzene [1a] – p. 94. This is of importance because of the danger of handling this highly toxic



(1)

substance, particularly at high temperature. The report of H.M. Inspector of Explosives [8] describes fatal accidents in South Africa on 29 February 1932, when an old explosive was carried out in sacks on the bare backs of a dozen natives. Two of them suddenly collapsed and one was taken ill. One of the men died a few hours later. Casualties were caused by the absorption of DNB through the pores of the skin.

The problem of toxicity of *m*-dinitrobenzene has attracted the attention of physicians for a long time. It has been found that animals poisoned with the compound developed methaemoglobinaemia, anaemia, liver damage, convulsions and cerebral paralysis [82, 83]. The problem of metabolism of *m*-dinitrobenzene in a living organism was examined and reviewed by Parke [84]. By using *m*-dinitrobenzene labelled with ^{14}C he examined the metabolism of the substance in rabbit and found that major metabolites in the urine were: *m*-nitroanaline and *m*-phenylenediamine (14% and 21% respectively) 2,4-diaminophenol (31%) and 2-amino-4-nitrophenol (14%). The minor products (present in trace quantity, below 1%) were: unchanged *m*-dinitrobenzene, 2,4-dinitrophenol, 4-amino-2-nitrophenol, *m*-nitrophenylhydroxylamine and derivatives of this: 3,3-dinitroazoxybenzene and *m*-nitrosonitrobenzene.

Electrochemical properties

The ease of reduction of the nitro group of aromatic nitro compounds suggested using aromatic nitro compounds for electrochemical cells. The electrochemical cell Mg/*m*-DNB seems to be particularly suitable giving a high yield of 160 Wh/kg. The reaction requires an acid or neutral medium [85].

Isomeric dinitrobenzenes

High purity *o*- and *p*-dinitrobenzene can be obtained by the oxidation of *o*- and *p*-nitroaniline respectively. The oxidation was carried out with hydrogen peroxide (30%) in acetic acid [36].

Some attention was paid to *o*-dinitrobenzene as an oxidizing agent (Chapter IV).

sym-Trinitrobenzene (Vol. I, p. 248)

Some new data have been published [1] on the physical properties of *sym*-trinitrobenzene such as vapour pressure between 122°C (m.p.) and 270°C.

A few more charge–transfer complexes have been described of *sym*-trinitrobenzene with: phloroglucinol and nitrophloroglucinol [9], picric acid [10], ferrocene [11].

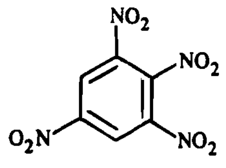
Although the compound possesses very good explosive properties an application could not be found for it owing to the difficulty of making it. A new laboratory method was given by Olah and Lin [12] of nitrating *m*-dinitrobenzene to *sym*-trinitrobenzene with nitronium tetrafluoroborate in fluorosulphuric acid solution. A short description of the method is given below.

Nitronium tetrafluoroborate and *m*-dinitrobenzene were added to fluorosulphuric acid and cooled in a dry ice/acetone bath. The temperature was gradually raised to 150°C. After three hours of heating the reaction mixture was poured on to crushed ice. The nitro product was extracted with dichloromethane, washed with sodium hydrogen carbonate solution and dried over magnesium sulphate. The yield of *sym*-trinitrobenzene was 61.6% with 5% unreacted *m*-dinitrobenzene.

The reaction time of 2.2 hours gave a 66% yield of *sym*-trinitrobenzene and 17% of unreacted substrate. A reaction time of 3.8 hours gave a 49.3% yield of high purity *sym*-trinitrobenzene.

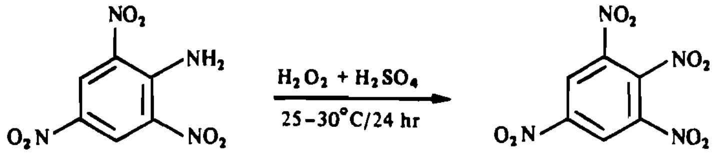
sym-Trinitrobenzene can be subject to a number of nucleophilic reactions. The known reaction for transformation of this compound into 3,4-dinitrophenol under the action of alkalis (Vol. I, p. 251, reaction 11) was facilitated by irradiation with ultraviolet [27, 28]. Pure 3,5-dinitrophenol without the azoxy compound resulted.

1,2,3,5-Tetranitrobenzene (Vol. I, p. 257)



m.p. 127-129°C

1,2,3,5-Tetranitrobenzene was obtained by a new method established by Nielsen and co-workers [13]. In general terms it consists in the oxidation of an amino group of polynitroanilines with concentrated (98%) hydrogen peroxide in 100% sulphuric acid. The reaction of picramide was carried out below 30°C with an excellent yield:



93%

(2)

According to Nielsen [16] the method consists in the action of peroxydisulphuric acid $H_2S_2O_8$:

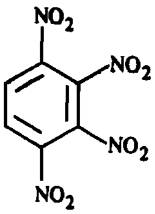
$$H_2O_2 + 2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H_2O. \tag{3}$$

Murto [14] examined the action of sodium ethoxide on 1,2,3,5-tetranitrobenzene. It produced a red colour attributed to the formation of a quinoid structure and eventually sodium picrate. A more detailed study of the action of nucleophiles on 1,2,3,5-tetranitrobenzene was made by Crampton and El Ghariani [15]. They obtained σ-complexes of Jackson–Meisenheimer type.

1,2,4,5-Tetranitrobenzene (Vol. I, p. 259)

Crampton and El Ghariani [15] examined the behaviour of 1,2,4,5-tetranitrobenzene (m.p. 188°C) towards nucleophile and found that σ-complexes were being readily formed. Nielsen and co-workers obtained [16] the same product of higher purity (m.p. 190–191°C) by the oxidation of 2,4,5-trinitroaniline with 90–98% H_2O_2 in oleum or 100% sulphuric acid.

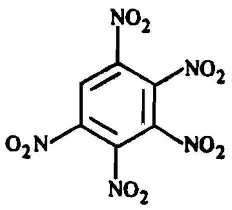
1,2,3,4-Tetranitrobenzene



m.p. 120–121°C

The new compound – 1,2,3,4,-tetranitrobenzene was obtained by Nielsen and co-workers [16] by the oxidation of 2,3,4-trinitroaniline with hydrogen peroxide (98%) in sulphuric acid (100%) at 10–18°C with a 78% yield. Oxidation with concentrated hydrogen peroxide in the presence of sulphuric acid forms a new modification of the method for the introduction of a nitro group, described earlier by Nielsen and co-workers [13], where no sulphuric acid was used.

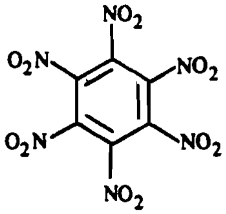
Pentanitrobenzene



m.p. 142–143°C

Tetranitroaniline (Vol. I, p. 560) was used by Nielsen and co-workers [13] to oxidize it with 98% H_2O_2 in the presence of 20% oleum at a temperature below 30° C. Pentanitrobenzene resulted.

Hexanitrobenzene (HNB) (Vol. I, p. 259)



m.p. 246-262°C

The method given in Vol. I could not be repeated. Also no data on the preparation were given and the only paper published until recently was on crystal structure [17] and some data on the properties [18]. It decomposes in air to yield trinitrophloroglucinol. Its density is *ca.* 2.0 and the rate of detonation (at $\rho = 1.9$) is 9500 m/s.

Nielsen and co-workers described in their remarkable papers [13, 16] the formation of hexanitrobenzene by oxidation of pentanitroaniline.

The reaction was carried out either (1) in fuming (20% SO_3) sulphuric acid at 25–30°C by adding 98% H_2O_2 or (2) in trifluoromethanesulphuric acid at 45–55°C with 90% H_2O_2. The product was extracted with dichloromethane and dried over magnesium sulphate (which also removed trifluoromethane sulphuric acid). Method (2) gave 90% yield.

A lower yield (58%) was obtained by method (1).

Also a relatively low yield was produced with potassium persulphate instead of hydrogen peroxide.

Wide range of m.p. is explained in terms of the formation of a few decomposition products in the course of heating near the m.p. of the substance. At 100° C nitro groups are transformed into phenolic groups yielding pentanitrophenol, tetranitroresorcinol and eventually trinitrophloroglucinol. In the absence of light HNB shows good stability at room temperature, but irradiation produces an interesting isomerization of nitro groups to nitrites which in turn are hydrolysed to phenolic groups [120]:

$$-NO_2 \xrightarrow{h\nu} -ONO \longrightarrow -OH$$

Other high nitrated derivatives of benzene obtained by the method of Nielsen [16]

The following were the compounds obtained by oxidation of the nitro derivatives of aniline:

1,2,3-trinitrobenzene (Vol. I),
1,3-difluoro-4,5,6-trinitrobenzene (m.p. 88–90°C)
1,3-difluoro-2,4,5,6-tetranitrobenzene (m.p. 99–100°C)
fluoro-pentanitrobenzene (m.p. 152–154°C)

The latter three compounds are new to the literature.

NITRO DERIVATIVES OF TOLUENE

Nitration of Toluene to Nitrotoluenes (Vol. I, p. 265)

Formation of nitrotoluenes is an important step in the manufacture of the trinitro product and has been the subject of some review articles: [19, 20] which were dedicated to the kinetics of mononitration.

Giles, Hanson and Ismail [19] found that in mononitration of toluene with a standard nitration mixture of nitric–sulphuric acid and water, the organic phase contained nitric and nitrous acids, but did not include sulphuric acid and water. The authors also studied the role of agitation. Their conclusion was similar to that reported previously [2] that mass transfer between the phases plays an important role, and a fast reaction takes place in a zone in the aqueous phase adjacent to the interface. It is important to know the diffusivity of the aromatic substrate in the aqueous phase which depends on the design of the nitrator. The paper by Strachan [20] also points out the importance of mass transfer in agreement with a previously described statement (Vol. I, p. 49).

As has been already pointed out (Vol. I, p. 265) and Chapter III, in the mononitration of toluene, nitrocresols are formed [21]. They can be further nitrated to yield trinitrocresol and oxidized to oxalic acid. The presence of trinitrocresol is most undesirable (formation of sensitive salts) and therefore mononitrotoluenes should be washed with alkali to remove the nitrocresols (Vol. I, p. 359).

Some efforts have been made to reduce the proportion of undesirable *m*-nitrotoluene. A general rule is that the lower the temperature of nitration the smaller the proportion of *meta* isomer (Vol. I, p. 273). Also the use of nitric acid acetic anhydride mixture at 0°C can assure a lower proportion of *m*-nitrotoluene, for example to reduce it to 1.6% [22]. This is in agreement with former findings (Vol. I, p. 274).

Isomer control in the mononitration and dinitration of toluene was studied by Harris [23, 24]. Both papers were dedicated to the increase of *p*-nitrotoluene which is an important intermediate in dyestuffs and pharmaceuticals manufacture, where both *o*- and *m*-isomers are waste products and the high proportion of 2,4-dinitrotoluene is desirable for isocyanate production. This aim was achieved by adding phosphoric acid to the nitration mixtures.

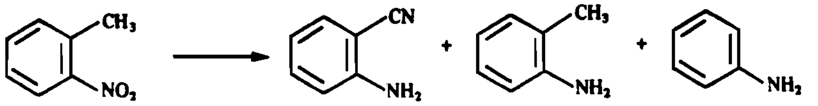
A number of papers (in addition to those mentioned in Vol. I) were given by Kobe, R. M. Roberts and co-workers [122–125] on the determination of the isomer distribution of the nitration of *o*-, *m*- and *p*-nitrotoluenes by the method of isotope dilution analysis.

The nitration of toluene to trinito products will be presented in a separate paragraph.

Mononitrotoluenes

A few unexpected reactions of nitrotoluenes have been recorded in recent years. Such is the reaction described by Hakanson and Nielsen [25] of the oxidation of *o*-nitrotoluene with dilute (35%) nitric acid at 190°C to yield (30%) picric acid. On the contrary *m*- and *p*-nitrotoluenes yield *m*- and *p*-nitrobenzoic acids. In addition to picric acid also nitro- and dinitrobenzoic and 3,5-dinitrosalicylic acids were formed. A large quantity of nitrogen was evolved and this led the authors to rationalize the reaction as passing through the formation of a diazo compound.

o-Nitrotoluene under action of ammonia in the presence of catalysts (Si-Mo-V-Bi-Base) at elevated temperature (4) was converted to *o*-cyanoaniline in addition to aniline and the expected *o*-toluidine.



(4)

INDUSTRIAL METHODS OF MONO-NITRATION OF BENZENE AND TOLUENE (Vol. I, p. 232 and Vol. I, p. 275)

Industrial methods of mono-nitration of benzene and toluene are either periodical or continuous. More attention is now given to continuous methods – safer and more economic when applied to a large, continuous production. Nevertheless, periodic nitration is still in use for smaller and less regular production.

Matasă and Matasă [29] in their monograph collected technical data on the nitration of benzene and toluene (Table 26).

TABLE 26. Mononitration

Components*	Benzene Nitrating acid	Benzene Spent acid	Toluene Nitrating acid	Toluene Spent acid
HNO_3	32	1	28	1
H_2SO_4	60	83	56	69
H_2O	8	15	16	29
NO_2	–	2	–	2
Temperature °C	40		60	
Reaction time min.	60		75	
Ratio HNO_3: hydrocarbon	100:100		100:100	
Yield in % of theoretical	98		97	

* In weight per cent.

Removal of Phenolic By-products

To free the aromatic mononitro products from phenolic by-products the usual industrial procedure consists in washing the nitro compound with water to free it from acids and then washing with dilute sodium hydroxide (concentration 1–5% NaOH and an excess of 5–15%). The process is efficient as regards to purification of the nitro compound but produces a considerable amount of water containing sodium phenates and is an obnoxious effluent. This can be dealt with by acidification and extraction of phenols with organic solvent inmiscible with water (such as benzene or more costly solvents). The method is expensive and led to the search for another method. Hanson and co-workers [30] developed a method of extracting phenolic compounds with a weak basic reagent such as phosphate salts. A mixture of trisodium and disodium hydrogen phosphate, for example 64.2 g/l of $Na_2HPO_4 . 2H_2O$ with 21.9 g/l of $Na_3PO_4 . 12H_2O$. After separation from the purified nitro compound the aqueous solution of phosphates and sodium phenates is mixed with benzene which dissociates the phenates and the liberated phenols are dissolved in benzene. The main constituent (*ca.* 80%) of phenolic fraction is 2,6-dinitro-*p*-cresol.

Periodic Nitration

Little can be added to the design of periodic nitrators as given in Vol. I, p. 155 (contrary to the continuous nitrators). An interesting innovation (which can also be used in continuous nitrators) deals with the control of the efficiency of stirring as given in the monograph by Chekalin, Passet and Ioffe [31]. It consists of a U-shaped glass tube on the lid of the nitrator. The tube is connected with a steel tube reaching the bottom of the nitrator (Fig. 16). The U-tube is filled with a coloured electrolyte solution and connected to an electric circuit. When the stirrer is in motion the pressure inside the nitrator increases and this is manifested by the difference of the levels in the U-tube. As a consequence the electric circuit is disconnected. When mixing stops (or is inadequate) the levels in the U-tube equalize, the circuit is closed and an acoustic or light signal gives a warning.

The emulsion of the nitro product and spent acid enters a separator which is designed on the principle of a laboratory separating funnel [31].

The nitro compound forms the upper layer. The spent acid is taken through the bottom valve and switched to another container when the upper layer appears in the 'lantern' situated just above the valve. The spent acid is further treated with a fresh hydrocarbon which goes to the nitrator and the nitro product is washed with aqueous alkaline solution to remove acids and phenols.

Continuous Nitration

The advantages of continuous method have already been pointed out in Vol.

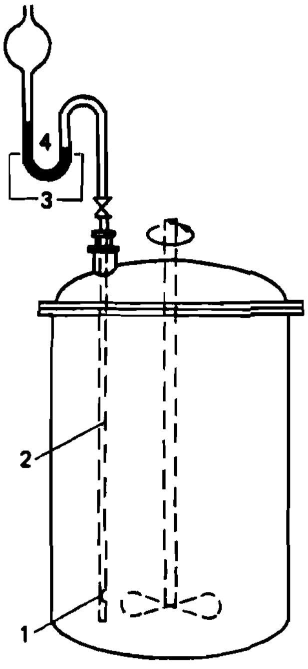


FIG. 16. Control of the efficiency of the stirrer according to Chekalin *et al.* [30]. 1 – Orifice in tube 2. 3 – electrodes, 4 – coloured electrolyte.

I, p. 366. It should be added that continuous nitration does not involve losses in time used for loading, emptying the nitrator and heating and cooling its contents as in periodic nitration. According to Soviet authors [31] the production of nitrobenzene can be increased 15 times, by changing periodic into continuous nitration.

One of the popular designs for nitrators was given by Biazzi (Vol. I, p. 108, Fig. 47), originally designed for the nitration of glycerine and adapted with small changes for the nitration of aromatic compounds.

SOVIET METHOD (ACCORDING TO CHEKALIN, PASSET AND IOFFE [31])

The following is a diagrammatic presentation of a continuous nitrator made of stainless steel (Fig. 17).

The hydrocarbon enters through the top of the central, wide diameter tube where it is cooled, driven down and at the bottom meets the nitrating acid. Through energetic mixing the emulsion is formed and driven upwards through the stainless steel tube. Continuous outflow of the emulsion is achieved from the upper part of the nitrator.

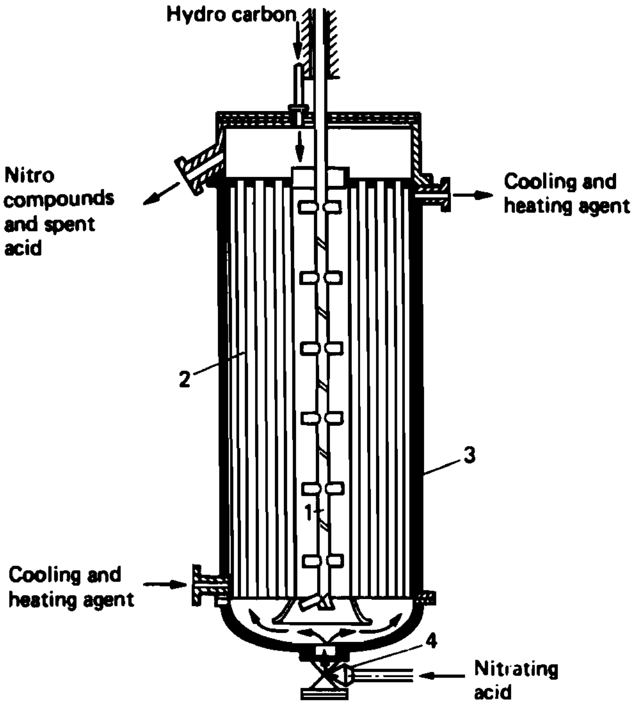


FIG. 17. Continuous nitrator according to Chekalin *et al.* [30]. 1 – Stirrer, 2 – tubular cooler and heater, 3 – stainless steel plate, 4 – regulation valve.

It is of great importance that the continuous nitrator should be completely air-tight.

The emulsion enters the continuous cylindrical separator – Fig. 18 near the middle of its height. The place of entrance is changed depending on the nitrated substance: it should correspond to the surface of the separation of phases.

The lighter nitro compound flows to the upper part of the cylinder and the heavier spent acid flows out through a syphon tube. It is advisable to fill the cylinder with Raschig-rings.

A general diagram of continuous nitration of benzene (and also toluene) according to Soviet sources (Chekalin, Passet and Ioffe [31]) is given in Fig. 19. The nitrator is provided with a cooling mantle, two cooling coils of different tube diameters, the stirrer has an upper turbine mixer driving the liquids downwards and a lower propeller. The supply of hydrocarbon, nitrating acids, spent acid and cooling liquid (usually water) is regulated in such a way as to keep the temperature of nitration at 65–68°C in the case of nitration of benzene. The concentration of nitrobenzene in the acid remains constant *ca.* 5%. The emulsion enters two spiral 'coolers' where the reaction is ended: 90% of nitric acid is used in the nitrator and 9–9.5% in the coolers, thus 99–99.5% of nitric acid is used for the

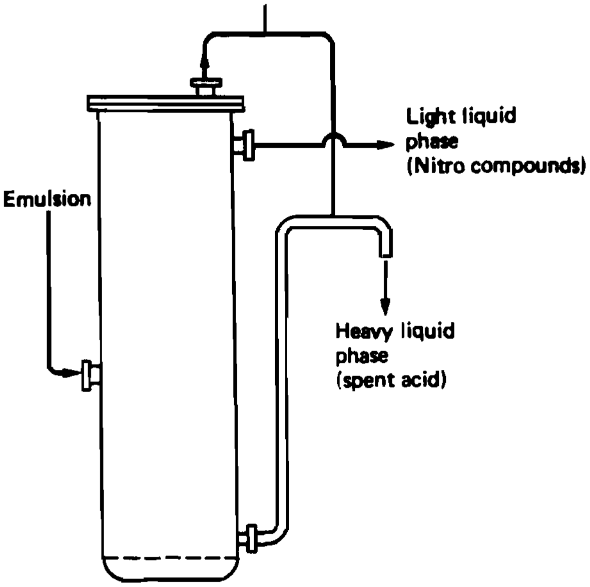


FIG. 18. Continuous separator according to Chekalin *et al.* [30].

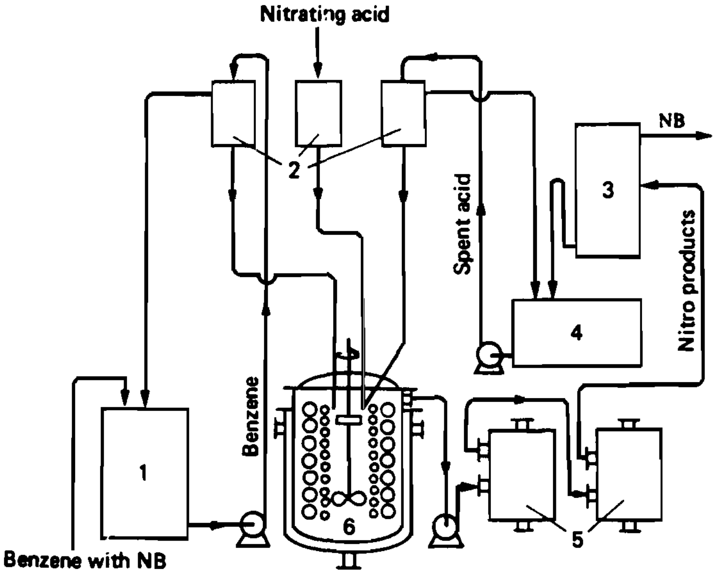


FIG. 19. General scheme of nitration of benzene or toluene according to Chekalin *et al.* [30]. 1 – benzene or toluene storage tank, 2 – measuring tanks for the hydrocarbon, nitration acid, spent acid, 3 – continuous separator, 4 – spent acid tank, 5 – spiral coolers, 6 – nitrator of continuous action.

nitration. In the second spiral cooler the reaction mass is cooled to 30°C. It should be understood that the spiral coolers are provided with stirrers. From there the emulsion enters the continuous separator. Due to the great difference of the density of nitrobenzene (or nitrotoluenes) and the spent acid, the separation takes 5–10 min.

Every 1000 kg of nitrobenzene gives 900–1000 kg of spent acid containing: 70–73% H_2SO_4, 1.5-2.2% nitrobenzene and 0.25–0.5% nitric acid. Nitrobenzene is extracted from the spent acid with benzene. The latter is partly nitrated with the residual nitric acid and the content of nitrobenzene and nitric acid after the extraction falls to 0.1–0.15% and 0.01–0.03% respectively. Benzene with a small quantity of nitrobenzene is sent to the storage tank and from there to the nitrator.

It is strongly emphasised that perfectly faultless automation is necessary for the safe and efficient process. Thus the ratio: hydrocarbon/acid is under automatic control according to the temperatures of the reaction, cooling liquid inflow is regulated according to the temperature of the cooling liquid leaving the nitrator. The cooling water entering the spiral coolers is also automatically controlled. If the mixing in the nitrator and supply of cooling liquid becomes inadequate, the flow of hydrocarbon into the nitrator is automatically stopped and the whole plant ceases to operate.

BOFORS-NOBEL-CHEMATUR METHOD OF NITRATING BENZENE AND TOLUENE TO MONONITRO PRODUCTS (FIG. 20) [32]

An innovation in the nitration technique was introduced by Bofors-Nobel-Chematur (Sweden). This is the so-called "Nitration Circuit". It consists in the ingenious use of a centrifugal pump as a nitrator. A cooler and a gravimetric separator are included in the circuit. Cooled acids and hydrocarbons are injected into the circuit. Hydrocarbons are: benzene or toluene used for the extraction of spent acid together with fresh hydrocarbons. The nitro compound and the spent acid overflow to the gravimetric separator and are split into streams of spent acid and a nitro compound. The spent acid is mixed with fresh hydrocarbon and subsequently the latter enters the circuit as mentioned above. The spent acid containing 70% H_2SO_4 is removed and can be used for fertilizer production or can be concentrated and recycled for nitration. The nitro compound is washed with dilute NaOH solution to remove phenols.

The advantages of the nitration circuit method are as follows: low oxidation due to the short contact time of the hydrocarbon with the acid, full nitric acid utilization, safety due to a very small quantity of the nitro compound in the circuit.

The following is the material balance given by Bofors-Nobel-Chematur (Table 27) [32]:

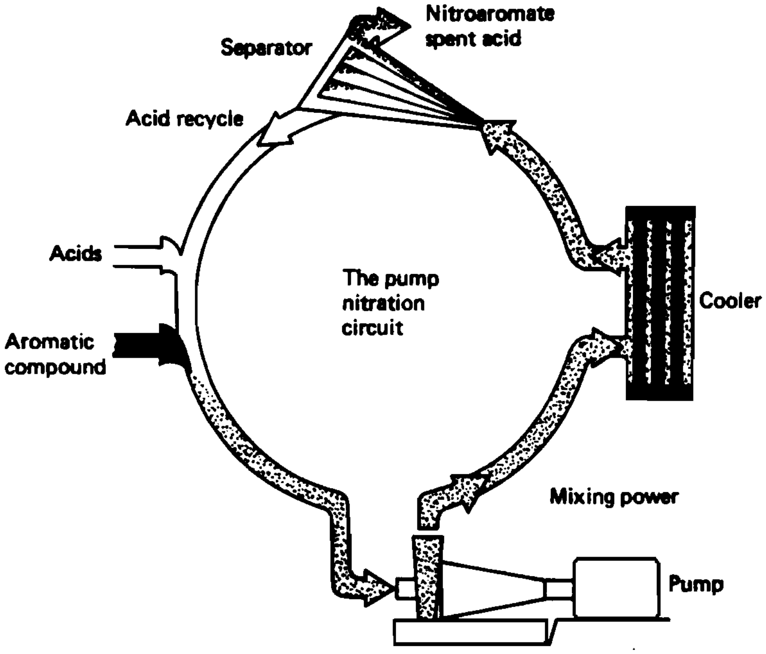


FIG. 20. Bofors-Nobel-Chematur. The Pump Nitration Circuit diagram. Courtesy Bofors-Nobel-Chematur.

TABLE 27. Consumption of materials in kg for production of 1000 kg of nitrobenzene and nitrotoluene

	Nitrobenzene	Nitrotoluenes
Hydrocarbon:		
benzene	650	–
toluene	–	686
Nitric acid 98% as 100% HNO_3	537	486
Sulphuric acid 96% as 100% H_2SO_4	460*	390*
Sodium hydroxide as 100% NaOH	5	10.4

* If the spent acid is concentrated the consumption is only 5% of the above figure.

DINITROTOLUENES (Vol. I, p. 281)

As is known dinitrotoluenes are not explosives by themselves but they are of course intermediates in the manufacture of TNT and are in use as ingredients of:

(1) mining explosives,
(2) some smokeless powders.

For mining explosives a low melting mixture of isomer is used. It is readily miscible with nitroglycerine and dissolves soluble nitrocellulose. For smokeless powder a relatively pure 2,4-dinitrotoluene is used. For further nitration, dinitrotoluene – a mixture (m.p. *ca.* 35°C) is used and after nitration to trinitroproduct, the latter is purified.

Physical (including thermochemical and explosive) Properties

The following are figures for main isomers of dinitrotoluene according to Meyer [1].

TABLE 28. Properties of dinitrotoluenes

	Dinitrotoluene 2.4-	 2.6-
Density	1.521 g/cm^3	1.538 g/cm^3
Melting enthalpy	26.1 kcal/kg	22.5 kcal/kg
Enthalpy of formation	−89.5 kcal/kg	−57.6 kcal/kg
Heat of detonation	−1056 kcal/kg	−1538 kcal/kg
Ignition temperature	360°C	
Volume of detonation gases	602/l/kg	
Lead block test	240 cm^3/10 g	

The same source [1] gives vapour pressure of the 2,4-isomer:

at	35°C	0.014 milibar
	70°C (m.p.)	0.111
	100°C	0.83
	150°C	8.5
	200°C	50.5
	300°C	300

The MAK-value (maximum permitted concentration in air at a workplace) is 1.5 mg/m^3.

The specification of commercial product is as follows:

moisture:	no more than 0.25%
benzene insoluble:	no more than 0.10%
acidity (as H_2SO_4):	no more than 0.02%
tetranitromethane:	absent
solidification point	
for smokeless powder grade:	68.0 ± 2.5°C
for commercial explosives:	liquid–solid mixture

Data for isomeric dinitrotoluenes are given in Vol. I, pp. 281–282.

Formation of Dinitrotoluenes from mononitrotoluenes (Vol. I, p. 285)

It is generally known that 2,4-dinitrotoluene is formed by nitration of *o*- and *p*-nitrotoluene and 2,6-dinitro isomer by nitration of *o*-nitrotoluene. It was accepted that 2,3-, 3,4- and 3,6-isomers are produced from *m*-nitrotoluene. Nevertheless it was firmly established that the nitration of *o*- and *p*-nitrotoluene can also produce a small proportion (below 0.5%) of 2,3- and 3,4-dinitrotoluene respectively [33]. Also small proportions of other isomeric dinitrotoluenes, such as 2,3-, 2,5- and 3,4- was proved from *o*- and *p*-nitrotoluene respectively [34]. Hill and co-workers [39] have found that the nitration of pure *o*- and *p*-nitrotoluene at −10°C with a nitrating mixture containing SO_3 yielded only 0.1% dinitro- and trinitroproducts deriving from *m*-nitrotoluene.

The formation of *m*-nitrotoluene derivatives from *o*- and *p*-nitrotoluene can be understood on the basis of the electron densities, free valencies and localization energies as depicted in Fig. 14. Also the formation of 3,5-dinitrotoluene seems to be possible by direct nitration of *m*-nitrotoluene [34].

The exact analysis of the nitration product has almost been perfected since the advent of chromatographic methods (t.l.c. and gas chromatography) and exact and reliable detection of isomers and impurities of lower and higher nitrated hydrocarbons [35–37] has been possible.

French authors [118] isolated pure isomeric dinitrotoluenes: 2,3, 2,5 and 3,4 from the product of the nitration of *m*-nitrotoluene by fractional distillation and repeated crystallization. 2,6-Dinitrotoluene was isolated by distillation of crude dinitrotoluene.

The following are setting points and distillation temperatures of isomeric dinitrotoluenes:

3,4	set pt. 58.3	, distilled under 10 mmHg	166–168°C
2,5	50.3	,	175–177°C
2,3	59.3	,	181–183°C

Recently 2,5-, 2,3- and 3,4-dinitrotoluenes were obtained by oxidation of 2-methyl-4-nitroaniline, 2-methyl-6-nitroaniline and 2-methyl-6-nitroaniline respectively [38]. The oxidation was carried out by hydrogen peroxide in acetic acid at 65–75°C. The yields were around 70% of theoretical.

As mentioned earlier low temperature nitration of toluene favours the reduction of the yield of *m*-nitrotoluene. This was examined in detail by Hill and co-workers [39]. They found that while lowering the nitration temperature from −5° to −35°C a reduction of 3,4-, 2,3- and 2,5-dinitrotoluenes occurred from 2.06% to 1.40% and the setting point of the product raised from 61.0 to 63.7°C. According to the same authors the use of trifluoromethanesulphonic acid with nitric acid made it possible to use a very low temperature on mononitration (−110° to −60°C) and the temperature 0° to 25°C on dinitration. When mononitration was carried out at −110°C and dinitration at 0° to 25°C, the content of isomeric dinitrotoluenes was as low as 0.33%. This figure is the lowest that has been recorded for dinitrotoluenes derived from toluene.

A problem was recently raised again on the production of high purity 2,4-dinitrotoluene not only because of its use in the manufacture of TNT but also for reduction to *p*-toluilenediamine which is an important starting material for polyurethane. The general tendency is to use high purity *p*-nitrotoluene to introduce the second nitro group. Thus Vinnik and co-workers [95], Leitman and Fedorova [96], found that the nitration of pure *p*-nitrotoluene produces pure 2,4-dinitro product. Nevertheless Ziółko and Matys [97] stated on the grounds of their experiments that the nitration of pure *p*-nitrotoluene yielded 2,4-dinitrotoluene containing 0.3–0.5% 3,4-dinitrotoluene. The conditions of the nitration were as follows:

Nitration acid contained	25%	HNO_3
	70%	H_2SO_4
	5%	H_2O.

An excess of the acid over theoretical was 5%, the temperature of nitration between 75 and 95°C. The yield of 96% of the product with setting point over 69.5°C was obtained. Crystallization from ethanol or trichloroethylene yielded practically pure 2,4-dinitrotoluene.

INDUSTRIAL METHODS OF DINITRATION OF BENZENE AND TOLUENE

Matasă and Matasă [29] collected the technical data on dinitration of mono nitro derivatives of benzene and toluene.

Modernized Pilot-plant and Industrial Production of DNT

Three modern methods of dinitration will be given here:

(1) Pilot-plant method by Haas and co-workers [40] of low temperature nitration of toluene,
(2) continuous method of Bofors-Nobel-Chematur two-step process with a pump nitrator [32, 41],
(3) continuous method of Biazzi S.A. [132].

Low Temperature Nitration of Toluene to DNT [40] – Fig. 21

The principle was based on the nitration of toluene by anhydrous mixtures composed of nitric acid and oleum at temperatures between 0° and −10°C (freezing point of the solution) [39]. The dinitration was nearly quantitative (over 99%) when the molar ratio HNO_3/toluene was 2.1–2.2. With the increase

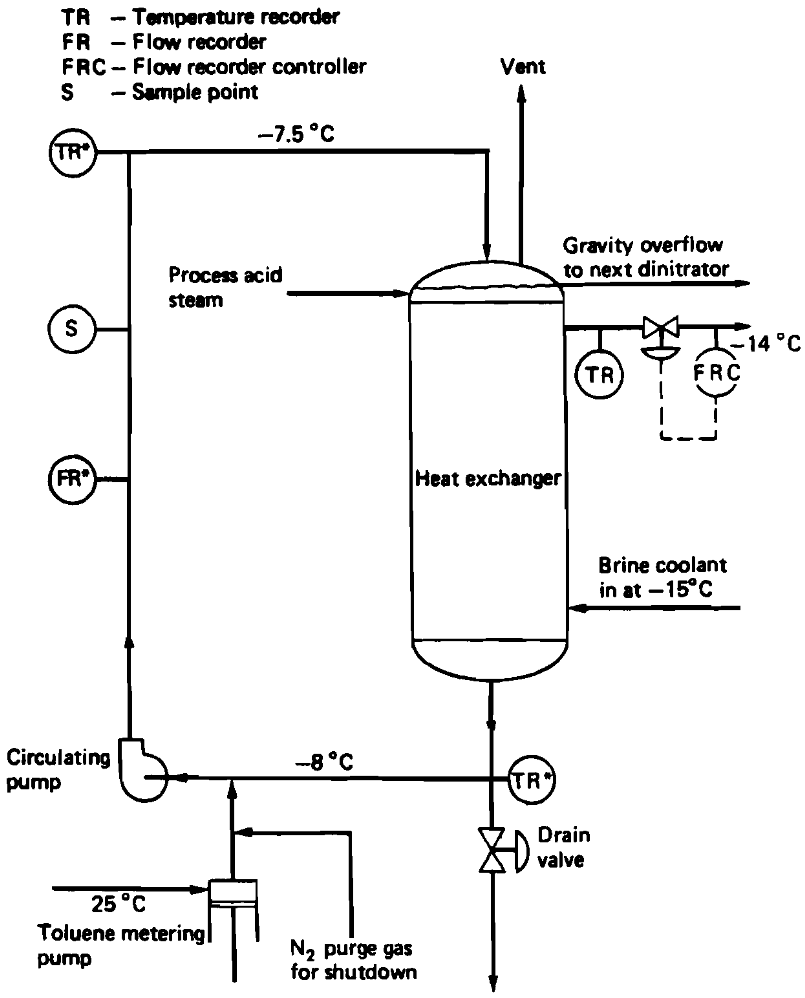


FIG. 21. Low temperature nitration of toluene to DNT according to Haas, Yee *et al.* [40].

of the ratio (e.g. to 4) the yield decreased (*ca.* 98%). The optimum was obtained with molecular proportion of reagents:

toluene	1.0
HNO_3	2.11
SO_3 (as 20% oleum)	1.97
SO_3/HNO_3 ratio	0.93

The yield at –10°C was 99.4%.

These experiments served as a basis for DNT pilot plant development [40]. Toluene has a low solubility in nitratic acid, subsequently, toluene is added just ahead of the centrifugal pump. Toluene is dispersed into the anhydrous acid at −8°C.

The dinitration is carried out in four recycle nitrators. The acid stream moves through the reactors and toluene is added to each of the first three. The effluent from the last nitrator has the composition in wt %:

dinitrotoluene	12.5
trinitrotoluene	5.5
HNO_3	0.2
H_2SO_4	68.9
nitrozylsulphuric acid	12.8
HNO_2	0.1

The effluent is heated from −8° to 35°C in a tank where the product is divided into two phases. The upper phase enters the trinitrator and the lower – acid phase is diluted with water to reduce the concentration to 70% H_2SO_4. The nitro compounds are separated and sent to the trinitrator and spent acid to the concentration unit.

The diagram of the system is given in the paragraph on trinitration.

Bofors-Nobel-Chematur Method of Manufacture of DNT (Fig. 22) [134]

This method is based on the principle of a circuit nitration pump for the production of nitrobenzene and nitrotoluene, as described already (p. 151). Each circuit is comprised of the nitration pump, cooler, separator and acid overflow vessel. The toluene fed to the mononitration circuit leaves the separator, is pumped as mainly mononitrotoluene to the dinitration circuit and leaves the separator as DNT ready for washing. The sulphuric acid fed to the dinitration step flows down-stream and leaves the mononitration circuit acid to overflow as

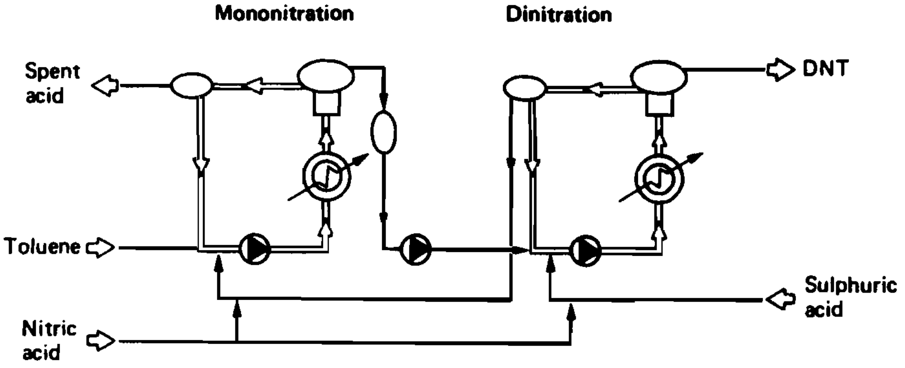


FIG. 22. Bofors-Nobel-Chematur method of manufacture of DNT (diagrammatic presentation). Courtesy A. B. Bofors-Nobel-Chematur.

spent acid. Nitric acid is fed to both circuits meeting the requirements of fully nitrated dinitro product and possibly complete consumption of nitric acid. The spent acid contains *ca.* 70% H_2SO_4 and less than 0.5% HNO_3 and does not require denitration.

An important innovation is the use of Bofors-Nobel centrifugal separator which minimizes the volume of the circuits and the size of the plant (Figs 23 and 24). It was originally designed in the 1960s for nitroglycerine manufacture, now it is accepted for DNT and TNT production. It changes the classical static separator, considerably reduces the amount of the explosive in the apparatus and is particularly suitable for use in continuous methods. It can be used to separate the nitro product from the spent acid and in the process of purification and washing of the nitro product. According to the manufacturer it can be easily cleaned. A relatively low operating speed of 500–1000 rpm is much below the critical figure. The separator can be installed in the nitrator – this design is described in the paragraph dedicated to the manufacture of TNT.

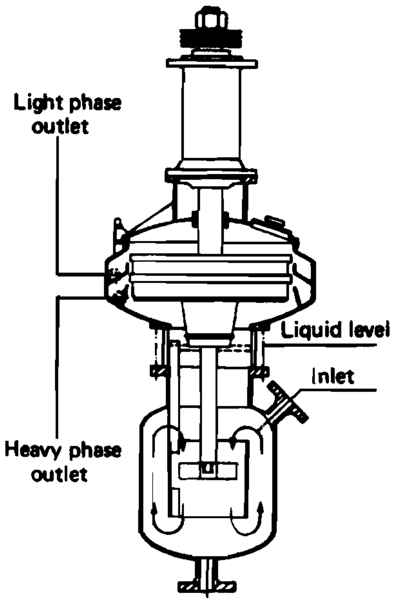


FIG. 23. Bofors-Norell Centrifugal Separator. Courtesy A. B. Bofors-Nobel-Chematur.

Biazzi S.A., Vevey Continuous Method [132]

The continuous Biazzi nitration process was used for the first time in 1935 for the manufacture of nitroglycerine. It soon became clear that many advantages were offered by this system such as the increased reaction speed, the high

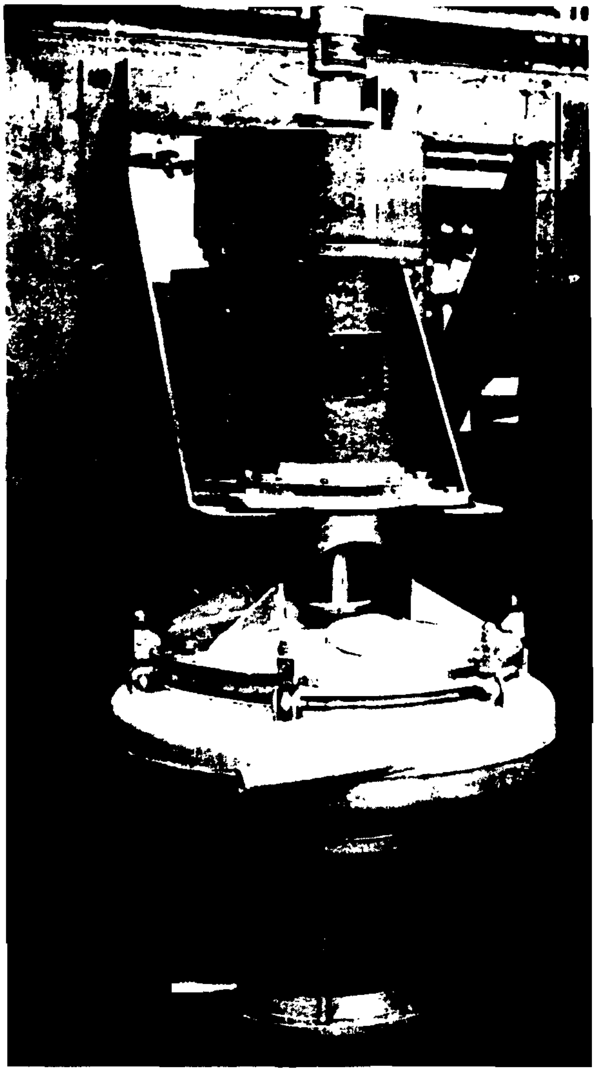


FIG. 24. Bofors-Norell Centrifugal Separator. General View. Courtesy A. B. Bofors-Nobel-Chematur.

heat transmission coefficient, the new method of separating the phases, washing by counter-current flow could be applied to the nitration of other organic products such as aromatic compounds.

A general scheme is presented in Fig. 25.

The reaction takes place in nitrators into which toluene and mixed acid is introduced continuously in exact proportion. The number of nitrators in the series varies from two to four. The temperature in each nitrator is kept constant

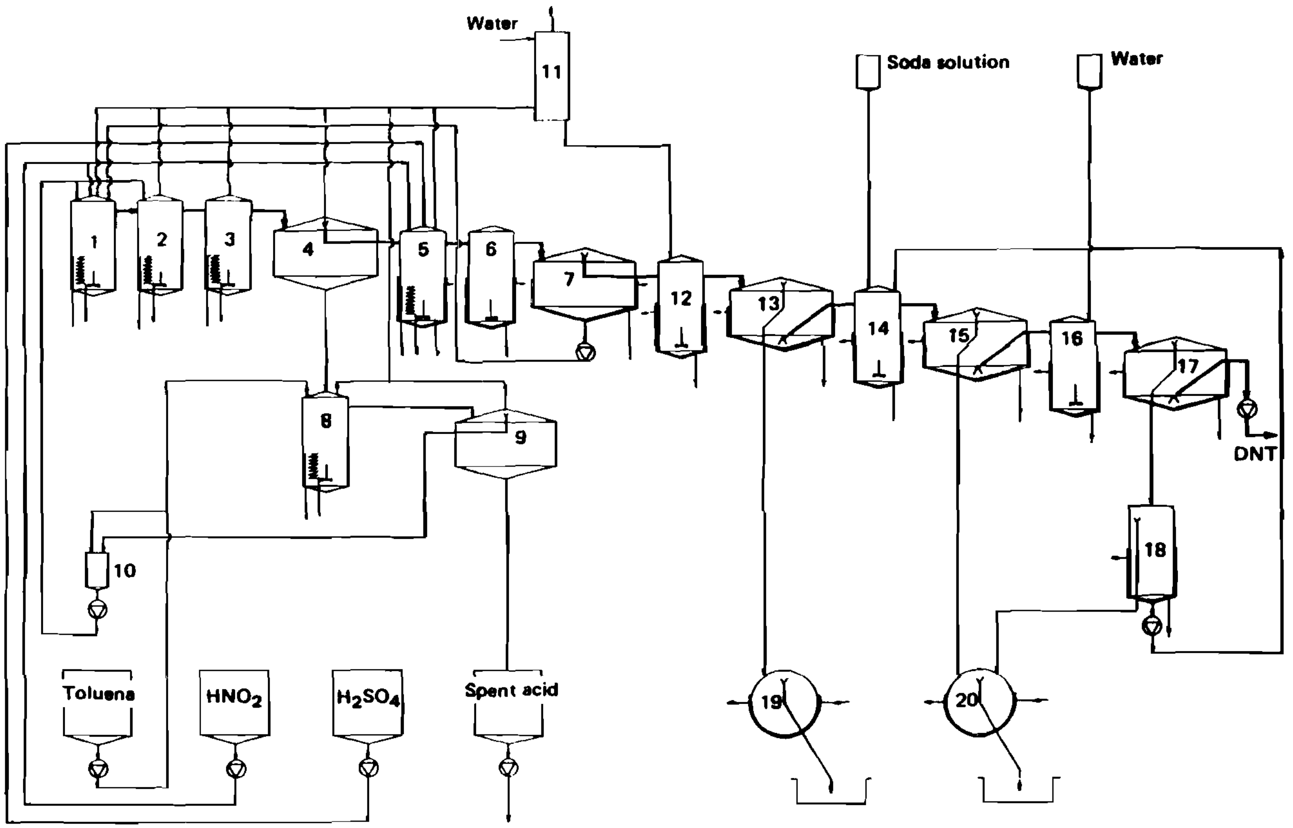


FIG. 25. DNT Biazzi S.A. plant for the manufacture of nitroaromatics. 1, 2, 3, Mononitrators; 4, MNT spent acid separator; 5, 6, Dinitrators; 7, DNT spent acid separator; 8, spent acid stripper; 9, final spent acid separator; 10, toluene feeding tank; 11, scrubbing column; 12, 14, 16, washers; 13, 15, 17, washing separators; 18, recycled waste-water feeding tank; 19, acidic waste-water catch tank; 20, alkaline waste-water catch tank.

by a thermostatic system. The stirring is achieved by a turbine acting as a pump. The emulsion from the nitrator enters a 'semistatic' Biazzi separator. The separated product is nitrated in next nitrators followed by a second separator.

The spent acid from the second separator is used as nitration acid for the previous stage.

The final spent acid is generally mixed with toluene to extract dissolved nitrobodies and use up the small remaining quantity of nitric acid.

The separated DNT is, washed with water, with an alkaline solution and finally with fresh water. The water from the last wash is used again for the next wash. Between each wash the product is separated in a Biazzi separator.

The plant is made of stainless steel.

The manufacturing parameters are kept constant by automatic remote control. Among recorded parameters is the Redox value of the spent acid fully described in Chapter XI. In case of any irregularity the plant is automatically stopped and an alarm given in the control room.

TRINITROTOLUENE (Vol. I, p. 290)

2,4,6-Trinitrotoluene (TNT) remains the most popular explosive because of its stability, low sensitivity to impact, friction and high temperature and well developed methods of manufacture. It is widely used in commercial explosives as a good sensitizer and is much safer in production and handling than nitroglycerine. For commercial explosives lower grade purity of TNT is being used whereas the military grade TNT must be a highly pure compound.

Physical (including thermochemical and explosive) Properties

The setting point of TNT for military purposes should not be lower than 80.2°C. Chemically pure substance shows 80.8°C. TNT recrystallized from nitric acid is commercially available, its setting point is 80.6–80.7°C [1a].

The following are figures related to properties of TNT according to Meyer [1].

Thermal conductivity of 2,4,6-trinitrotoluene was determined by Belayev and Matushko [43]: $\lambda \times 10^4 = 4.8$ cal/cm sec grade for pressed substance and 3.5 cal/cm sec grade for powder. The temperature conductivity $a \times 10^4 = 8.5$ cm^2/sec and 11.5 cm^2/sec respectively.

The following are data for the velocity of detonation calculated for the infinite diameter and density ρ [42]:

$$D_\infty = 1872.7 + 3187.2\,\rho$$

when ρ = from 0.9 to 1.5343.

At higher densities: $\rho = 1.5543 - 1.636$

TABLE 29. Properties of 2,4,6-trinitrotoluene

Density (crystals) 1.654, molten 1.47 g/cm^3
Melting enthalpy 23.1 kcal/kg
Specific heat at 20°C 0.331 kcal/kg
Enthalpy of formation −62.5 kcal/kg
Heat of detonation 1080–1210 kcal/kg
Ignition temperature 300°C
Volume of detonation gases 730–620 l/kg
Lead block test 300 cm^3/10 g
Impact sensitivity 1.50 kpm
Friction sensitivity – no reaction up to 36 kp
Critial diameter in steel tube 5 mm

Vapour pressure:

at 81°C (m.p.)	0.057 millibar
100	0.14
150	4
200	14
250 (beginning of decomposition)	86.5

$$D_\infty = 6752.5 + 3187.2\,(\rho - 1.53342) -$$
$$25102\,(\rho - 1.5342)^2 + 115056\,(\rho - 1.5342)^3.$$

The figures are valid for diameters from 0.7 to 7.8 cm. Meyer [1] gives 6900 m/s for $\rho = 1.60$.

The specification for commercial product is according to [1]:

Appearance: light yellow coloured flakes or crystals

Setting point for TNT of highest purity	min 80.6°C
for some commercial explosives	80.2 – 80.4°C
ammonium nitrate commercial explosives	various lower setting points
Volatiles	no more than 0.1%
Tetranitromethane	none
Acidity (as H_2SO_4)	no more than 0.005%
Alkalinity (as Na_2CO_3)	no more than 0.001%
Benzene insolubles	no more than 0.05%
Minerals (as ash)	no more than 0.01%

For a long time the setting point was the most common criterion of the purity of TNT. However, it has also been recognized for some time that it does not answer all the problems of the practical use of the explosive. One of the important problems is the exudation of a multicomponent eutectic mixture of isomeric trinitrotoluenes and dinitrotoluenes. Even a minute quantity of these substances can produce an inconvenience through the exudation.

This can occur in the course of the storage of projectiles with TNT particularly in summer time. The problem was recently reviewed by Reitsma [76]. Here are the main disadvantages produced by the exudation:

(1) it may affect the functioning of some components of the ammunition (e.g. initiators),
(2) cavities and cracks may be formed in the TNT casting and create a danger of premature detonation,
(3) the migration of explosive mixture to the screw thread of the fuse also creating a danger.

In the Federal Republic of Germany the exudation test consists in placing a cylinder of cast TNT on filter paper and keeping it at 70°C for 20 hours. The diameter is then determined by the stain on filter paper and also the loss of weight of the cylinder.

Reitsma examined different factors influencing the test, for example higher humidity favours the exudation. The test is not only influenced by impurities of TNT but also by the crystal size of the cast. Pressed cylinders of TNT do not show the exudation.

His conclusion is that the practical value of the test in its present form is limited.

Attention should be drawn to the microscopic examination of cast TNT. Thorpe and Connick [126] suggest polishing the cast sample with MgO powder and direct observation by reflected light. The previously suggested 'peal' method by Williamson [127] does not reveal sufficient structural detail.

Thorpe and Connick suggested:

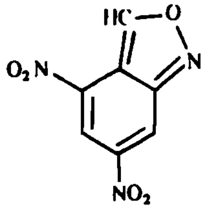
(1) preliminary polishing with wet silicon-carbide paper,
(2) intermediate polishing by hand on nylon velvet using MgO powder,
(3) finishing on vibratory polishing,
(4) an etch with bromoform shows up the grain orientation of the TNT matrix.

Among the properties of 2,4,6-trinitrotoluene related to its explosive character, very important is the sensitivity to high temperature. High sensitivity of molten TNT to impact was described in Vol. I, pp. 319–320.

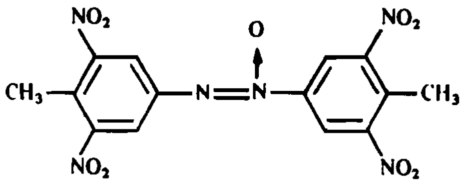
Another problem is its thermal decomposition. T. Urbański and Rychter [44] examined the decomposition at temperatures near 400°C and above. The energy of activation between 380–440°C was of the order of 14 kcal/mol. Between 490 and 750°C trinitrotoluene took spherical shape and decomposed slowly with the evolution of a considerable amount of soot. The energy of activation in the range of temperatures 490–750°C was of the order of 8 kcal/mol and the shape of the curve: induction period against temperature was analogous to that shown for nitroglycerine in Vol. II, p. 50, Fig. 13.

Kamlet and co-workers [45] undertook the task of elucidating chemical changes of 2,4,6-trinitrotoluene which occurred during its isothermal decomposition at 200°C. 75–90% of TNT remained unchanged after 16 hours. The main products were: 4,6-dinitroanthranil (I) (2–4%), 2,4,6-trinitrobenzaldehyde

(1–2%), 2,4,6-trinitrobenzyl alcohol (*ca.* 0.2%) and a minute amount (*ca.* 0.1%) of an azoxy compound of a probable structure (II).



I



II

Camera and Biasutti [121] developed an interesting method of isothermal pressure metering for the determination of chemical stability of aromatic nitro compounds, as described in Chapter IV. It showed that a temperature as low as 200°C could be dangerous if DNT pure, or with TNT, is kept for less than 24 hours (e.g. 18 hours) at this temperature.

Also the addition of many foreign substances to molten TNT can create a great danger (see the paragraph on safety of manufacture and handling aromatic nitro compounds).

The formation of an azoxy compound is not surprising considering the ease of transformation of nitro compounds into benzazoxy derivatives. Among them is known an important by-product of the continuous methods of making TNT known as 'white substance' (p. 169). A few unidentified products of oxidation and reduction were isolated, all of which had high melting points. In up to 13% a polymeric substance was formed, insoluble in benzene, which did not melt below 300°C and burned when ignited by a flame. The substance was named 'explosive coke'. No *sym*-trinitrobenzene was found by Kamlet *et al.*, contrary to the statement by Rogers [46]. Kamlet suggested that a minor quantity of TNB could be produced through the oxidation of TNT to trinitrobenzoic acid followed by a loss of CO_2 (the usual reaction leading to TNB) and after that TNB was lost in the 'explosive coke'.

An important finding of Kamlet and co-workers was that at 210°C a spontaneous self-ignition of TNT occurred after 14–16 hours (or less) of heating.

The thermal decomposition of TNT is accompanied by the formation of free radicals. Jantzen [108] found free radicals at 240°C.

Hara, Kamei and Osada [109] described a detailed study of the thermal decomposition of TNT. They examined the decomposition by differential thermal analysis, thermogravimetry, infra-red spectroscopy, ESR and mass spectrometry. One of their most important findings was that TNT produced free radicals already in the vicinity of the melting point, that is 80°C. The substances which promote the decomposition of TNT are free radicals which are stable at room temperature. They are insoluble in benzene or chloroform and are partly oxidized polymeric substances.

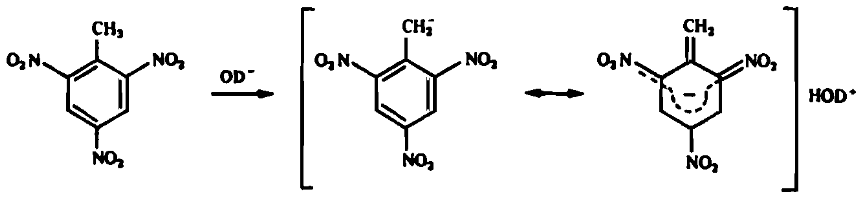
Chemical Properties of 2,4,6-Trinitrotoluene

Acid properties. The acid properties of 2,4,6-trinitrotoluene were discussed in Vol. I (p. 300). This problem was reviewed with the reactions of the formation of σ-complexes (Chapter IV). Acid properties were also examined by modern methods. Thus Schaal [47] gave the following figures for pK_a of trinitrotoluene, as compared with dinitrotoluenes:

2,4,6-trinitrotoluene	pK_a = 14.45
2,4-dinitrotoluene	17.12
2,6-dinitrotoluene	19.00

Therefore, 2,6-dinitrotoluene is the weakest acid.

Buncel and co-workers [48] also came to the conclusion that 2,4,6-trinitrotoluene has acid properties. They based it on their report of a ready exchange of CH_3 protons of the compound in basic medium of deuterium oxide:



(5)

Fyfe, Malkiewich and Norris [94] examined intermediates formed by the action of bases on TNT using high resolution NMR spectroscopy. Within 0.5 sec of mixing equimolar proportions of TNT and methoxide in DSO and CH_3OH the Jackson–Meisenheimer complex is formed. It decayed over 8 sec and the spectrum of anion according to (5) slowly appeared.

Salts of TNT were described in Vol. I, p. 304. A patent [79] claimed the use of salts of TNT for delay compositions.

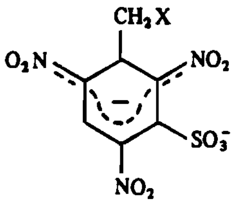
Action of light. This was described in Chapter V on the photochemistry of nitro compounds.

Reaction with Sodium Sulphite

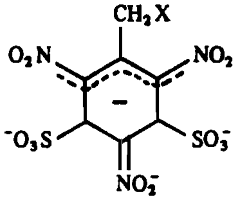
Reaction of 2,4,6-trinitrotoluene with sodium sulphite was extensively studied and reviewed by Crampton and co-workers [49], Strauss [50], Buncel and co-workers [51], Bernasconi and co-workers [52].

σ-Complexes with sulphonic groups are the products of the reaction of 2,4,6-trinitrotoluene (X = H) or trinitrobenzyl chloride (X = Cl) with one and two moles of sodium sulphite at 25°C: IIIa and b respectively.

According to Crampton [49b, d] dimethyl sulphoxide stabilizes the adduct 1:1. The compounds are soluble in water with a deep colour (440–460 nm and 550 nm).



III a



III b

The reaction of sodium sulphite with unsymmetrical trinitrotoluenes is much more vigorous replacing *meta* nitro with sulphonic group (Vol. I, p. 332).

Oxidation of 2,4,6-Trinitrotoluene

Kamlet and co-workers [53] made an interesting and important observation that the oxidation of 2,4,6-trinitrotoluene with dichromate-sulphuric acid in the presence of nitric acid gave a high yield (*ca.* 85%) of picric acid, that is the methyl group is replaced by phenolic group, whereas the oxidation with pure dichromate-sulphuric acid yields, as known (Vol. I, p. 255), 2,4,6-trinitrobenzoic acid. The formation of picric acid was rationalized according to Kamlet as the result of oxidative aromatic nucleophilic substitution which passes through the intermediate formation of 2,4,6-trinitrobenzoic acid.

Thus, the oxidation of 2,4,6-trinitrobenzoic acid with dichromate – 20% oleum in acetic acid solution yielded 71% picric acid.

Using acetic acid instead of nitric acid Kamlet *et al.* [53b] was also able to obtain picric acid from 2,4,6-trinitrotoluene. The yield was 70% by using chromium trioxide-sulphuric acid in acetic acid medium.

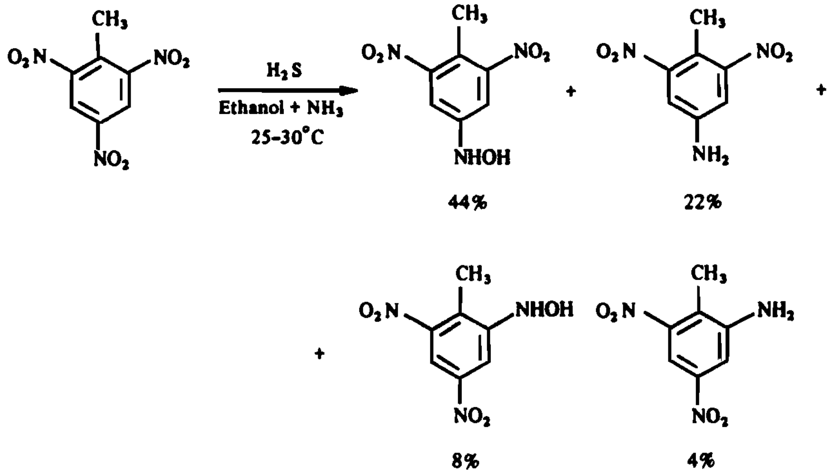
The oxidation of 2,4-dinitrotoluene [53a] with sodium dichromate in sulphuric acid in the presence of nitric acid yielded up to 45% of picric acid together with *ca.* 18% of 2,4-dinitrobenzoic acid. These authors found that 2,4-dinitrotoluene is more sensitive than 2,4,6-trinitrotoluene.

The oxidation–reduction process is involved in the formation of the 'white compound', a by-product of continuous production of TNT [54]. The formation of this compound is discussed in the paragraph on by-products of nitration of toluene to TNT.

Reduction of 2,4,6-Trinitrotoluene

An extensive study of the reduction of 2,4,6-trinitrotoluene was made by Nielsen, Coon and co-workers [55]. They also reviewed the existing literature. So far the use of different reducing agents produced mainly 4-amino-2,6-dinitrotoluene. Nielsen, Coon *et al.*, examined the use of hydrogen sulphide in the presence of a catalytic amount of ammonia and found the reaction to be solvent dependent: in dioxane both 4-amino-2,6- and 2-amino-4,6-dinitrotoluenes being formed. In ethanol the attack at position 4 is favoured but incomplete reduction to hydroxylamine derivatives also occurred.

The results can be summarized as follows (6):



(6)

Methylation of 2,4,6-Trinitrotoluene (Vol. I, p. 212)

In addition to the reaction of methylation reported by Fieser (Vol. I, p. 212), a more recent observation was reported by Sauermilch [56]. It consists in warming 2,4,6-trinitrotoluene and *sym*-trinitrobenzene with an aqueous 50% solution of acetic acid and Ce(IV) ammonium nitrate. At 90–95°C an evolution of CO_2 occurred with the formation of 2,4,6-trinitro-*m*-xylene with yields of 67% and 84% respectively.

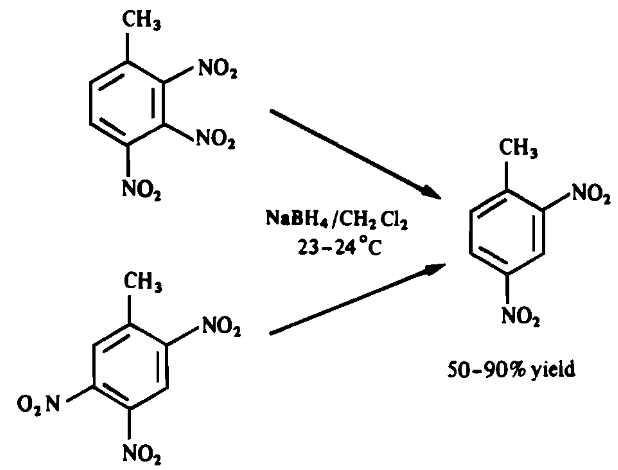
By using propionic acid instead of acetic acid nitro derivatives of ethylbenzene resulted.

Unsymmetrical Isomers of Trinitrotoluene and By-products of Nitration of Toluene

A number of analytical papers have been dedicated to the detection of isomers of trinitrotoluene and by-products by gas chromatography [57], NMR [58] and by TLC [59].

Some new reactions have been reported of unsymmetrical trinitrotoluenes. Okamoto and Attarwala [60] described the reaction of denitration of *meta* nitro group by acting with sodium borohydride in the atmosphere of nitrogen at 23–24°C in CH_2Cl_2.

Another extensive paper on the reaction of unsymmetrical trinitrotoluenes with ammonia leading to aminodinitrotoluenes was that by Nielsen, Coon and co-workers [55]. The main purpose of this work was to identify the major com-

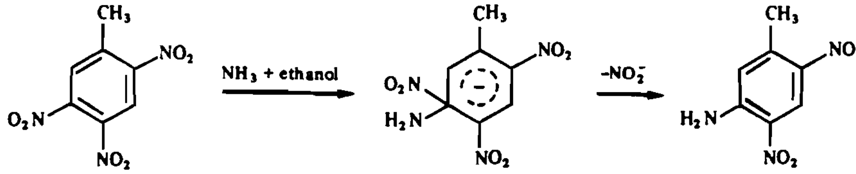


(7)

ponents of waste waters which are formed through ammonolysis and reduction of TNT isomers, and to determine their toxicity.

The method of Hepp (Vol. I, p. 331) was also used: the action of ethanolic solution of ammonia.

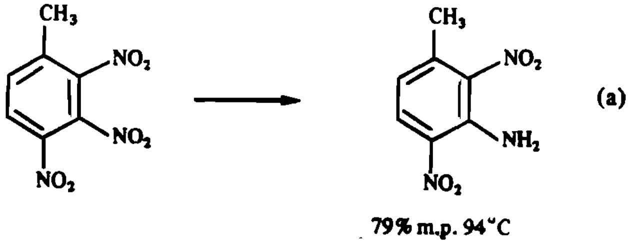
The mechanism consists of the initial formation of σ-adduct followed by splitting off NO_2 group in the form of the anion NO_2^- as depicted in scheme (8). It is referred to as the main unsymmetrical product – 2,4,5-trinitrotoluene:



(8)

The other isomers reacted in a similar way (9) with the exception of 2,3,6-isomer which gave a mixture of isomers.

Some of the aminodinitrotoluenes can be made by nucleophilic amination of 2,6-dinitrotoluene with hydroxylamine in basic medium [61, 62].



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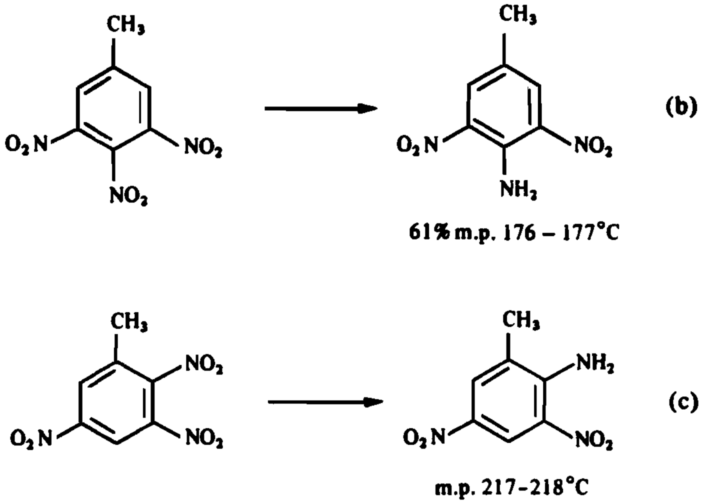

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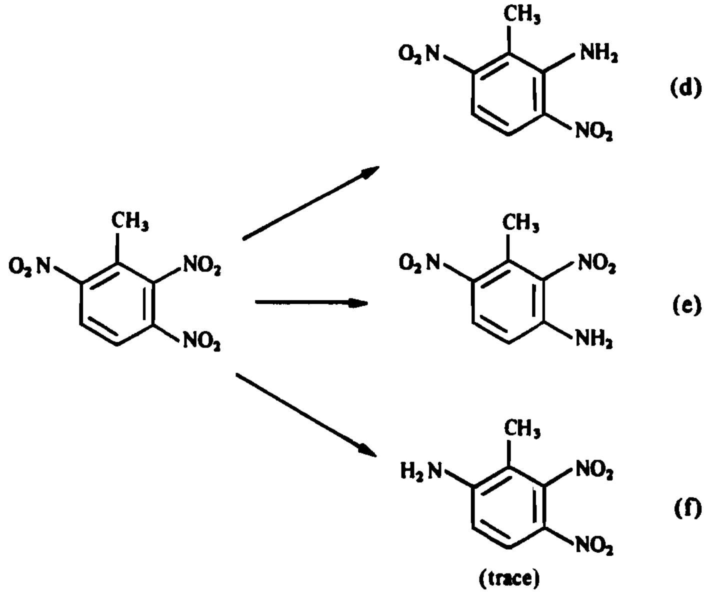

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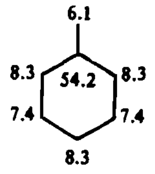
Tetranitromethane (TNM) (Vol. I, p. 337)

An important work was carried out by chemists of Picatinny Arsenal [63] who elucidated the problem of which part of the molecule of toluene is responsible for the formation of tetranitromethane.

Using carbon-14 as a tracer it was found that most TNM originates from the aromatic ring carbons with over 50% being contributed by the ring carbon attached to CH_3 group. The distribution of carbon atoms taking part in the formation of TNM is given in diagram IV.



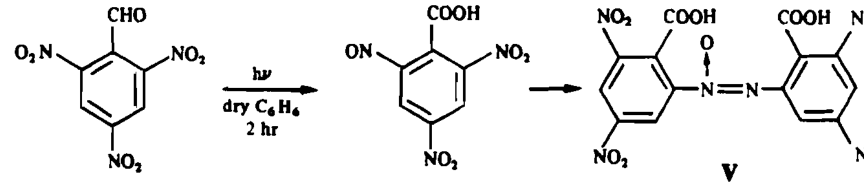
IV

It was found that over 80% of all the TNM can be traced to the dinitrotoluene isomers deriving from *m*-nitrotoluene. The ultimate formation of TNM is attributed to DNT oxidation reactions in competition with the reaction of nitration.

White Compound

It was found as early as 1950 that continuous methods of making TNT produce an as yet unknown compound named 'white compound'.

It was characterized by high m.p., white colour and a low solubility in nitrating acids. It readily crystallized out in various parts of the apparatus. Joshi and Patwardhan [54] established its structure as being 2,2′-dicarboxy-3,3′,5,5′-tetranitroazoxybenzene (V). They established it by synthetic route from 2,4,6-trinitrobenzaldehyde which was subjected in the light to the known reaction of Ciamician and Silber (Chapter V) yielding 2,4-dinitro-6-nitrosobenzoic acid. The latter on warming with water gave V (10):



V

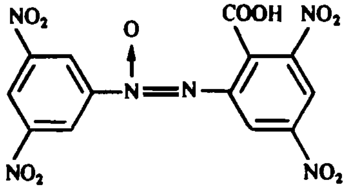
m.p. 245°C d.

(10)

The synthetic product was identical to that produced by continuous nitration.

The structure of V was confirmed by Kamlet and co-workers [53]. Kotarski, Krasiejko and co-workers [64] also confirmed the structure V given by Joshi and Patwardhan by using infra-red, NMR spectroscopy and mass spectrography. Recently Ziółko, Krasiejko and Dębowski [65] established that 'white compound' exists in two crystalline forms differing by their m.p.: 268–269°C and

239–240°C. The raw product is also accompanied by a monocarboxylic azoxy compound (VI) [53b] which can further be decarboxylated to tetranitroazoxybenzene while boiling in ethylene glycol [65].



VI

m.p. 205-206°C

Ziółko and co-workers [65] established the solubility of white compound in organic solvents, in nitrating mixtures and spent acids: Tables 30 and 31.

White compound is soluble in aqueous (5%) sodium carbonate and in 10% solution of Na_2SO_3 at 90°C. Sulphuric acid does not precipitate the substance from the latter solution.

TABLE 30. Solubility of white compound in organic solvents (in 100 g of solvents)

Solvent	Temperature (°C) 20°C	 Higher
Acetone	13.55	15.40 at 40°
Ethanol	6.80	7.85 at 50°
Benzene	0.0003	0.04 at 75°
Toluene	0.018	0.081 at 95°

TABLE 31. Solubility of white compound in water and acids (in 100 g of solvents)

Solvent		Temperatures (°C) 20°	 70°
Water		0.22	0.393
Sulphuric acid (96%)		0.433	0.581
Nitric acid (91%)		0.162	0.189
Nitration acid:			
HNO_3	41.5%	0.201	0.417
H_2SO_4	54.5%		
H_2O	4.0%		
Spent acid:			
HNO_3	0.2%	0.026	0.099
H_2SO_4	79.7%		
H_2O	20.1%		

The white compound was examined by the same authors with regard to its sensitivity to impact and high temperature.

The results are as follows:

Sensitivity to impact is of the order of that of PETN and much above TNT, thus:

5 kg from a height of 10 cm gave 100% explosion,
and 2 kg from a height of 25 cm gave 100% explosion
(the figures for PETN are: 10 cm and 23 cm respectively)

At 300°C the explosion occurred after 10 s,
320°C the explosion occurred after 5 s
(the figures for TNT are 95 and 60 s respectively).

An attempt was made to establish in which stage of nitration white compound is formed. According to de Cazanove and co-workers [66] the amount of white compound increases with the time of the reaction. Ziółko, Krasiejko and Dębowski [65] established that white compound composed mainly of V with a possible admixture of VI is formed in the course of trinitration and is dissolved in the acid which passes to di- and mononitration. There, in more dilute acids it is precipitated in various parts of nitrators, pipes, valves etc. The precipitate can disturb the regular trend of the process.

It is advisable to determine the presence of white compound in the products of nitration of toluene. It is also advised [65] to use the TLC technique on silica-gel: the solution of nitro compounds in acetone is put on the starting line and the chromatogram is developed with vapours of benzene–acetone–methanol–dioxane (50:5:30:15 vol.%). The chromatogram is treated with ethylene diamine solution in acetone (50/50). White compound can be detected as a magenta coloured spot of $R_f = 0.68$. (Nitro derivatives give a reddish-brown coloured spot at $R_f = 0.80$).

IMPURITIES OF TNT

As previously mentioned, Yasuda [59] examined TNT by TLC. Among unsymmetrical trinitrotoluenes he found dinitrotoluenes: 2,4-, 2,6-, 2,5- and 3,5.

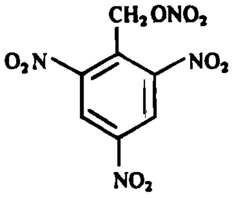
Gehring [67] undertook the task of examining non-volatile impurities of TNT by NMR technique. He found compounds in crude TNT as given in Table 32.

None of these substances were detected in purified TNT in quantities over 0.03%.

Special attention should be paid to 'α-Nitrato-TNT' which appears to have been detected by Yasuda [59], but no structure was given. Gehring [67] suggests the structure (VII):

TABLE 32. Impurities of crude TNT [67]

The substance	Quantity present in TNT in weight %
2,4,5-TNT	1.80–2.20
2,3,4-TNT	1.50–1.70
2,3,6-TNT	1.25–1.40
2,3,5-TNT	0.05–0.06
2,4-DNT	0.20–0.25
α-Nitrato-TNT	0.30–0.35
2,4,6-Trinitrobenzoic acid (TNBA)	0.20–0.22
2,4-Dinitrobenzoic acid	0.05–0.06
3,4-Dinitrobenzoic acid	0.01
2,4,6-Trinitrobenzaldehyde (TNBal)	0.20–0.24
m-DNB	0.003–0.005



VII

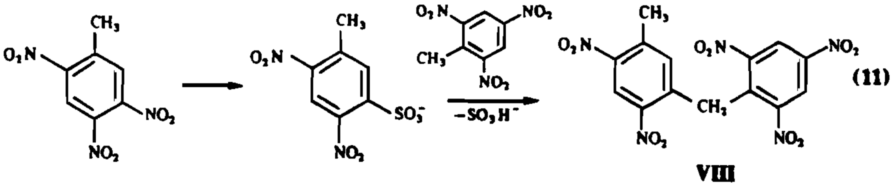
Kohlbeck and co-workers [68a] detected by TLC: trinitrobenzaldehyde, trinitrobenzylalcohol, hexanitrobibenzyl and azoxybenzene derivatives related to the 'white compound': tetranitroazoxybenzene and dimethyltetranitroazoxybenzene.

Sulphitation of Crude TNT ('Sellite' Process)

As known (Vol. I, p. 332) the reaction of sodium sulphite with unsymmetrical trinitrotoluenes is a major reaction in the purification of crude TNT, known under the name of 'Sellite Process' – 'sellite' being the name of sodium sulphite solution. Sodium sulphite solutions have pH > 8.0. It is known how sensitive higher nitrated aromatic compounds are to bases and sodium sulphite (particularly at a temperature, for example, above 40–45°C) can produce a damaging effect on TNT. It is therefore advisable to add a certain amount of sodium bisulphite to sodium sulphite to keep the pH value as low as possible. According to Clift and Fedoroff [71] 0.1–0.3% $NaHSO_3$ was added in the U.S.A. as a buffer to keep the pH value down.

By-products Formed in the Course of Purification of TNT with Sodium Sulphite

The excellent paper by Chandler, Kohlbeck and Bolleter [68b] has drawn attention to the possible formation of the 'new' by-products in the course of sulphitation of crude TNT ('sellite purification'). The authors noted a high reactivity of sulphonic group in *meta* position which derives from the sulphitation of unsymmetrical trinitrotoluenes. They explain the formation of 3-methyl-2,4,4',6,6'-pentanitrodiphenylmethane (MPDM) (VIII) from 2,4,5-trinitrotoluene by the reactions (11):



(11)

Another impurity previously reported [67, 68a] is 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB):

The same authors [68b] also reported the difference between the quantity of both products – MPDM and HNBB – in continuous and batch processes of the manufacture of TNT:

	Continuous methods:	Batch processes:
MPDM	0.1–0.3%	0.06%
HNBB	0.1–0.5%	0.01%

Industrial nitration of toluene to trinitrotoluene (Vol. I, p. 312) is described in the next paragraph.

Utilization of Dinitrosulphonic Acids Formed in Sellite Process
(Vol. I, p. 389)

In the widely used sellite process vast amounts of aqueous sulphite effluents ('red waters') are present. Some efforts were made to recover the compounds and at the same time to remove them from red waters, as they are harmful to the environment.

Red water is alkaline (pH 8.4) [98] and the products dissolved, slowly decompose on standing. Stabilization was achieved by acidifying with 25% sulphuric acid, allowing to stand for one week and then filtering [99]. The filtrate was extracted successively with benzene and ether and the solvent was evaporated. The precipitate from filtration and solid from evaporation amounted to 0.47% of the weight of the red water and proved to be mainly 2,4,6-trinitrotoluene. The stabilized (acidified) red water contains *ca*. 20% dissolved substances:

inorganics	5–8%
dinitrotoluene-sulphonic acids	4.5%
'Red Tar'	8.5%

According to Hall and Lawrence [99] Red Tar is composed mainly (90%) of sulphates. Gilbert [98] found that *ca*. 60% is composed of 2,4-dinitro-5-sulphonic and 40% of 2,4-dinitro-3-sulphonic acid.

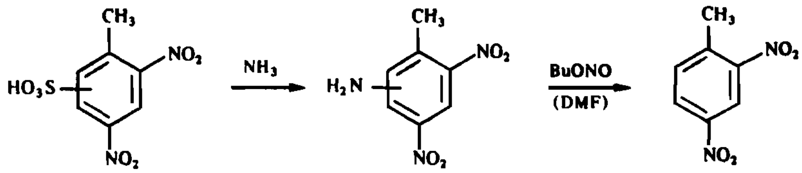
In another series of experiments [98] desulphonation was carried out on dinitrosulphonic acids. It is known that aromatic sulphonic acids can be desulphonated by heating with aqueous sulphuric and phosphoric acid but the data for dinitrosulphonic acid are very controversial and it appears that dinitrosulphonic acid cannot be readily desulphonated [98].

Subsequently reductive desulphonation was tried by methods which do not involve the reduction of nitro groups. A small yield (*ca*. 5%) was obtained [100] of 2,4-dinitrotoluene on desulphonation of 2,4-dinitro-5-sulphonic acid with sodium borohydride.

Reductive desulphonation was reported for 2,6-dinitrobenzenesulphonic [101] and 2,4,6-trinitrobenzenesulphonic to *m*-dinitrobenzene [101] and trinitrobenzene [102] respectively. In both reactions *N*-benzyldihydronicotinamide (the nicotinamide co-enzyme) was used.

Among the most important methods of transformation of the sulphonic group the following were reviewed by Gilbert [98].

Amination with ammonia under pressure [103] (12):

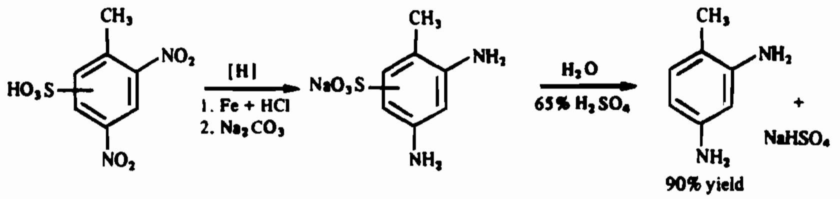


(12)

This method seems to be too expensive owing to the use of butyl nitrate as a diazotization and reduction agent. Substitution of the sulphonic group with hydrazine [104, 105] gave poor yield and was not economically justified owing to the expensive hydrazine.

Substitution of SO_3H with chlorine by reacting with $POCl_3$ and then removing chlorine with copper. The method was described for 2,4,6-trinitrobenzene [106] and 2,4-dinitrobenzenesulphonic [107] acids but it does not give the desired results with dinitrotoluene sulphonic acids [98].

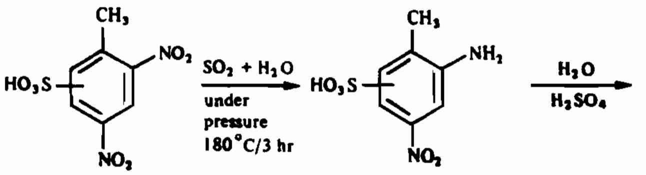
More promising is the reduction of the nitro groups followed by hydrolysis of the sulphonic group [98] (13):



(13)

Reaction (13) may possess a commercial significance owing to the value of *m*-toluylenediamine as a starting substance for urethane manufacture.

Another promising reaction is the partial reduction of the dinitro compounds followed by hydrolysis of the sulphonic group [98] (14):



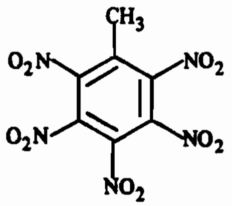
(14)

The reaction was tried with stabilized red water. The yield was 43% of the reacted sulphates present in the waters.

Recently a work has been reported on the treatment of red water with surfactants containing amino and quaternary ammonium groups which can form insoluble products with TNT (and probably with sulphonic acids salts formed in the course of the sellite process) [75].

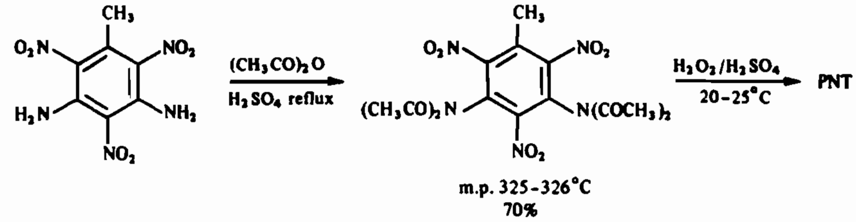
So far an adequate economic solution for the problem of utilization of sulphonic acids present in red water has not been found (see manufacture of TNT by Bofors-Chematur method [72] p. 177).

PENTANITROTOLUENE (PNT)



m.p. 225-240°C

The compound was prepared by Nielsen, Coon and co-workers [16] by oxidation of 3,5-bis (diacetylamino)-2,4,6-trinitrotoluene in 30% oleum with 90% hydrogen peroxide at 20–25°C (15):


(15)

3,5-Diamino-2,4,6-trinitrotoluene was made according to the improved method of Palmer [69].

The wide range of melting points of HNB and PNT has recently been explained by Coon [110] as the result of the isomerization of some of the nitro groups in the course of melting ($NO_2 \rightarrow ONO$). Subsequently a lower melting mixture occurred.

TNT MANUFACTURE (Vol. I, p. 345)

Continuous methods are now prevalent in the industrial methods of the manufacture of TNT. A general tendency is to use:

(1) relatively low temperature,
(2) high concentration of acids.

The first requirement ensures less by-products and particularly those produced by oxidation, and the second can help to obtain higher yield at lower temperature.

Nevertheless, batch processes are still in use. Matasă and Matasă [29] give parameters for the trinitration of dinitrotoluene – Table 33.

TABLE 33. Trinitration of dinitrotoluene

Composition of the acid	Nitrating mixture	Spent acid
HNO_3	49	1.5
H_2SO_4	49	92.0
H_2O	2	4.0
NO_2	–	2.5
Temperature °C	110	
Ratio HNO_3: DNT	120:100	
Yield in % of DNT	92	

It should be mentioned here that a paper on the nitration of DNT to TNT by anhydrous nitrating mixtures was given by Heertjes as early as 1953 [70]. He used nitric acid mixed with 40–72% SO_3 and a very good result was obtained by using the composition of the nitrating acid:

45–58% SO_3
51–28% HNO_3.

With an excess of 103% HNO_3 (i.e. 203% HNO_3 as compared to theoretical 100%) he obtained a yield of 98% while the temperature of nitration was kept at 81°C on mixing for 100 min, followed by heating at 109°C for a further 210 min.

Bofors-Chematur Continuous Method

The Bofors-Chematur method is now widely in use in many parts of the world. It emerged from Swedish–Norwegian Chematur and Norsk Spraengstoffindustrie (Vol. I, p. 371) incorporated by Bofors in 1968 [72].

The principle was given in Vol. I, but it is being continuously improved, the present process includes:

(1) nitration,
(2) washing with water ('presellite washing'),
(3) washing with sodium sulphite and bisulphite ('sellite purification'),
(4) 'post sellite' washing,
(5) drying,
(6) flaking.

1. Nitration. Raw materials: toluene or *o*-nitrotoluene, nitric acid (98% and 55%) oleum and sulphuric acid are stored in tanks from which they are fed to the process by metering pumps.

Nitration can start from toluene or *o*-nitrotoluene, *p*-nitrotoluene being isolated as an important intermediate for dyes and medicinal products – (Vol. I, p. 277). Nitration is carried out continuously in a series of nitrators through which the toluene or *o*-nitrotoluene and the nitrating acids flow in a countercurrent. In front of the first nitrator is placed an extraction vessel (not shown on the diagram) in which the residual nitric acid and nitro compounds are extracted from the spent acid by toluene. After extraction, the spent acid/toluene mixture enters the cooling unit. Toluene which now contains some nitrotoluene and acid is separated from the spent acid and enters the nitrator. The spent acid is sent for distillation.

All nitrators, extractors and spent acid coolers are equipped with 'dynamic' separators which have been described above – Fig. 23.

2. Presellite washing. TNT is continuously washed, in several washing vessels, by pure water to remove the acids. The washers are equipped with dynamic separators. The waste water, known as 'Yellow Water' is either sent to the washing system or to the absorbers, retaining the acids and organic products.

3. Sellite purification. The TNT is continuously treated with sellite solution in a series of washers. The pH level is controlled by pH meters. The washers are equipped with dynamic separators. The waste water, called 'Red Water' is transferred to a special destruction unit where water is evaporated and the remaining organic material is burnt.

4. *Post sellite washing*. The purified TNT is treated continuously in a washing system with pure water. The washers are equipped with dynamic separators. The waste water is transferred to Sellite purification. The washed TNT is transferred either in water emulsion or in molten form to the drying unit.

5. *Drying*. TNT is dried by heating with steam to 85–90°C and passing hot (75°C) air to agitate the molten substance.

6. *Flaking*. The dried TNT flows by gravity to the flaker which is a standard apparatus (Vol. I, p. 380, Fig. 38). It consists of an iron or steel drum rotating at constant speed and cooled inside by cold running water. By regulating the depth of immersion of the drum in the molten TNT the thickness of flakes can be controlled.

Design of Nitrators equipped with Centrifugal Separators.

The centrifugal separators which are usually given as an addition to the nitrators or washers (Fig. 23, 24), can be installed inside the reactor or washer. This is depicted in Fig. 26. It can be used for the capacity of the nitrator below 1250 kg/hr.

TABLE 34

The raw materials required for the production of 1000 kg of TNT are:

Toluene	485 kg
Oleum 20%	2250 kg
Nitric acid 55% and 98% calculated as 100%	1100 kg
Sodium sulphite	65 kg
Sodium bisulphite	10 kg
Sulphur dioxide	1 kg
Energy consumption per 1000 kg TNT are:	
HT Electricity and LT Emergency	135 kWh
Cooling water 28°C	50 m^3
Cooling water 15°C	50 m^3
Steam	1150 kg
Processed water	2 m^3

Low Temperature Process for TNT Manufacture

Haas, Yee and co-workers [40] developed a method of low temperature production of TNT. The main features of the method consist of:

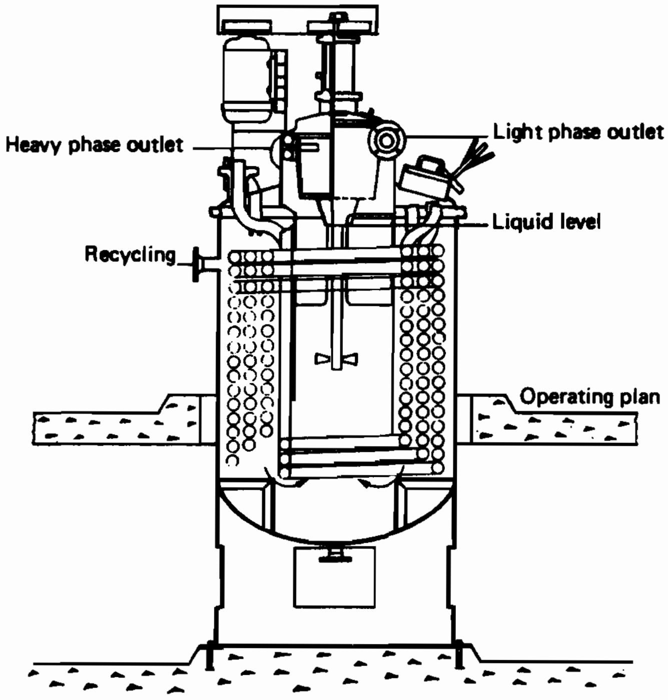


FIG. 26. Bofors-Norell Centrifugal Separator installed in a reactor. Courtesy A. B. Bofors-Nobel-Chematur.

(1) co-current flow of single phase the anhydrous acid and the nitro compounds,
(2) low temperature (−10°C) of dinitration,
(3) crystallization and filtration of TNT from the anhydrous nitrating acid.

A diagram of the system is given in Fig. 27. Dinitration has already been described and a diagram of the nitrating system given in Fig. 21. Trinitration occurred at 90°C, below 60°C it was insignificant, at 90°C the complete reaction of trinitration of DNT occurred at a batch process in *ca*. 1 hour. At 90°C an excess of oxidation occurred. The following feed material is added at a continuous rate to produce *ca*. 22 kg TNT/hr:

93 kg/hr of mixed acid,
85 kg/hr of dinitroeffluent containing DNT,
13 kg/hr of DNT from the dinitrator.

The composition and flow rate in the continuous method are given in Table 35.

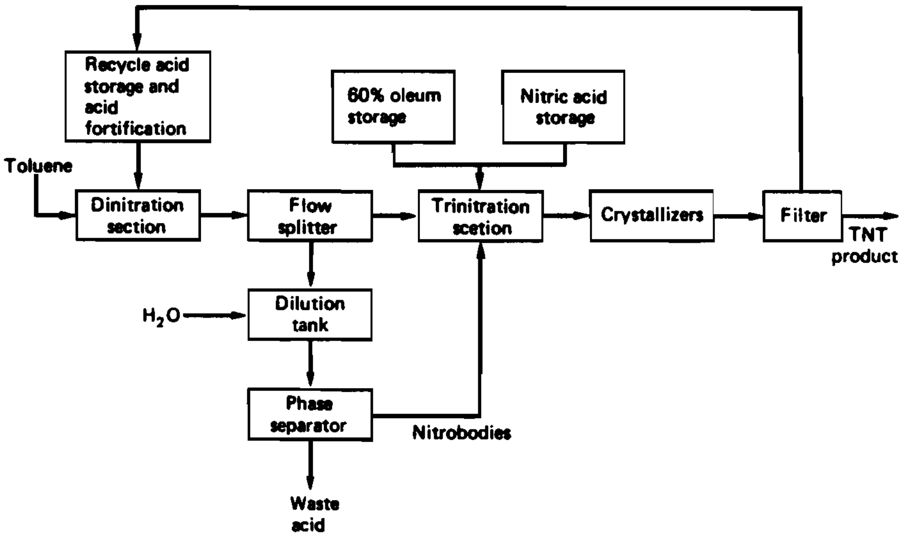


FIG. 27. Diagram of low temperature TNT process, according to Haas, Yee *et al.* [40].

TABLE 35. Composition of trinitration effluent

Compound	Flow kg/kg TNT	Wt %
TNT	1.4	16.5
HNO_3	0.65	7.7
H_2SO_4	4.6	54.3
SO_3	0.8	9.5
$NOHSO_3$	1.0	12.0

Crystallization. A diagrammatic presentation of the process is given in Fig. 28. The solvent was the trinitration acid of the composition: 10.6% HNO_3, 75.8% H_2SO_4, 10.6% SO_3. The solubility at different temperatures is collected in Table 36.

The process is diagrammatically depicted by a scheme – Fig. 28. The first three vessels are cooled with water of 50, 30 and 10°C and the last two with a brine containing 25% $NaNO_3$ at temperatures of −5 and −15°C. The acid for the crystallization should not be too cold, as it would produce crystals which were too small and could block the pipes connecting the vessels.

The acid flowing from the crystallizer contains *ca.* 5.3% dissolved TNT and *ca.* 9.7% HNO_3 the rest being sulphuric acid, SO_3 and nitrosylsulphuric acid. It passes to the first (hot) crystallizer, after the draining of TNT, it is washed with 70% sulphuric acid, followed by washing with water.

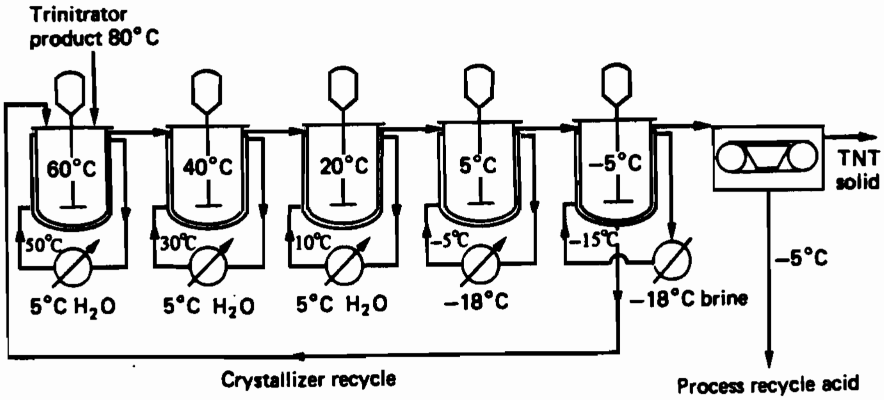


FIG. 28. TNT pilot crystallization unit, according to Haas, Yee *et al.* [40].

TABLE 36. Solubility of TNT in the trinitration acid

Temperatures	Dissolved concentration wt %
70	17.1
60	14.7
45	10.8
25	7.75
0	5.8
−10	5.3
−30	3.65

The filtrate removed from TNT contains *ca*. 66% of nitric and sulphuric acid and SO_3 used for the trinitration and is recycled to trinitration after the addition of acids.

Manufacture of TNT in the U.S.A. during World War II

Fedoroff [73] reviewed the methods of the manufacture of TNT in the U.S.A., after the description was declassified in the late 1960s. Some parts of the description possess an historical significance, but can create a good insight into the development of technology of one of the most important explosives.

One-stage Nitration of Toluene

During World War I, one stage nitration of toluene to TNT was carried out using a Hough nitrator (Vol. I, p. 157, Fig. 31). The nitrator was filled with

25,000 lb of the nitrating mixture (no composition was given). Toluene (2500 lb) was slowly introduced through a spray at 50°C. Gradually the temperature was raised to 110°C. The total time was 3 hours giving 5300 lb of TNT (85% yield).

Two-stage Process of Nitration

This method was in use at the Barksdale, Wisconsin plant, of the du Pont Co., the only TNT factory in the country between the two world wars. It consisted of mononitration and combined bi-tri-nitration.

Mononitration: toluene in a very thin stream was introduced to mono-mix for 3 hours at *ca.* 57°C. The charge was 'cooked' for 1 hour and then settled to separate mono-oil from the acid.

Combined bi-trinitration: mono-oil was added very slowly to a mixed acid containing 16% HNO_3, 82% H_2SO_4 and 2% H_2O. The ratio acid/mononitro was 9.5. During 2.5 hours of mixing, the temperature gradually rose to 120–125°C. The separated crude tri-oil was washed by agitating with hot water, dried and purified by crystallization with carbon tetrachloride.

Three-stage Process

This method was used from 1941 at Glen Wilton, Virginia and did not deviate from, at that time, the existing practice. The mono-nitration and di-nitration were carried out with the spent acids of dinitration and trinitration respectively mixed with 60–62% nitric acid. Mononitration was usually carried out in two stages to avoid the vigorous reaction of toluene with nitric acid. The idea was similar to that used in Germany (Vol. I, pp. 357–359). In Glen Wilton toluene was 'pre-mixed' in a mononitrator with a large quantity of acid composed of 7% HNO_3, 55% H_2SO_4 and 38% H_2O. After that mononitration acid was added to complete the nitration. The spent acid from mononitration was sent to the 'Recovery House' where nitric acid was distilled off (see Chapter on Denitration).

Trinitration was achieved with mixed acid composed of 97–100% nitric acid, sulphuric acid and oleum. It contained *ca.* 60% H_2SO_4, *ca.* 40% HNO_3 and a small amount (*ca.* 0.3%) of NO_2.

Direct Nitration Process

The so-called 'Direct Nitration' method was developed during 1942–45 in Beloeil, Quebec under collaboration between Canadian Industries Ltd and du Pont Co. (It was erroneously described [74] as being placed in Plum Brook Ordnance Work.)

This is a three stage process using essentially the method with three concentrations of mixed acid. The factory in Beloeil was making over 450,000 t of

TNT per month. Later in 1942 another factory in Keystone Ordnance Work, U.S.A. started using exactly the same method as that in Beloeil. The main data on the method can be seen in Tables 37, 38, 39 and 40.

The advantages of the 'new' method called 'Direct Nitration' are given below.

1. Better heat control is possible, because the addition of toluene to 7–8 times its mass of nitrating acid, allows more efficient dissipation of heat of re-

TABLE 37. Compositions of acids

Type of acid	HNO_3	H_2SO_4	Nitrosyl-sulphuric acid	Nitro compounds soluble in ether	H_2O	Density at 25°C
Mononitration	14.2	48.2	16.6	1.8	19.2	1.68
Spent acid after mononitration	3.5	55.7	16.8	0.3	24.0	1.67
Dinitration	13.0	54.3	16.9	9.0	7.8	1.78
Spent acid after dinitration	4.4	62.4	15.8	2.7	14.7	1.78
Trinitration						
1. Oleum	4.9	103.7	0.3	–	–	1.95
2. 'Semi-mix'	62.0	43.0	0.3	–	−5.0*	1.83
3. Final Composition	23.3	82.7	0.4	0.2	−6.2*	1.93
Spent acid after trinitration	3.4	63.5	17.6	13.5	2.0	1.87

* Maximum amount of water which can be added to obtain a mixture free of water. It can be used as a criterion of the concentration of water in the acid mixture.

TABLE 38. Main parameters of the nitration

	Weight ratio	Temperatures of nitration (°C)	Time of nitration (min)
Mononitration	Acid/Toluene 7.8	1. 35–38° 2. 54–57° cooling to 38°	40–45
Dinitration	Acid/MNT 3.7	1. 82° 2. 84–86° cooling to 65°	45
Trinitration	Acid/DNT 2.4	1. 79–80° 2. 90–91° 3. 110–111° cooling to 93–96°	90

TABLE 39. Material balance in 'direct nitration' at Keystone, June 1945

Yield of TNT in kg for 100 kg of toluene	209.84 kg
Raw materials for 100 kg TNT	
Toluene	47.66
Sulphuric acid	211.67
Nitric acid	145.19
Sellite*	10.29
Sodium carbonate	5.02
Acid consumed and lost for 100 kg TNT	
Nitric acid consumed and lost	105.72
Nitric acid recovered	37.45
Sulphuric acid lost	1.72
Sulphuric acid recovered	209.95
Mean setting point of TNT	80.4

* Sodium sulphite.

TABLE 40. Acid consumption and losses per 100 kg toluene

Nitric acid in mononitration	90 kg
Nitric acid in dinitration	90 kg
Nitric acid in trinitration	125 kg
Sulphuric acid	450 kg

action in the large mass of high specific heat acid, than was possible in the methods where a small amount of low specific heat toluene was used. The difficulty in the nitrator at the beginning of mononitration, was partially overcome by mixing the toluene, prior to nitration, with large amounts of cyclic acid, and in cases of trinitration by mixing the bi-oil with oleum.

2. The time cycle of nitration is considerably shortened by using the new method, because the addition of a small mass of toluene or oil to a large mass of acid in the nitrator, obviously requires less time, than the addition of a large amount of acid to a small amount of toluene or nitrated oil, as in the older processes.

3. The new method is safer, because even with a rapid increase in the temperature of nitration the possibility of formation of gaseous explosives mixtures is very slight. These gases consist of toluene vapours (or volatile nitro compounds) mixed with air or tetranitromethane. They accumulated in the dead space above the nitrated material and could be ignited by a spark of static electricity or local overheating due to the too rapid feeding of acid, thereby causing very dangerous explosions. Two such explosions are described in the chapter dedicated to accidents in the manufacture of nitro compounds.

The new method is also safer because there is practically no accumulation, on the surface of the acid layer, of large quantities of unnitrated organic compounds. Every new portion of organic substance introduced under the surface of acid, nitrates almost completely, except in trinitration, before it rises to the surface. If the feed is too fast and the temperature starts to rise above permissible limits, overheating may be easily checked by simply halting the addition of organic substance. Also the proportion of organic compounds to acids at any time during nitration, except at the end of nitration, is much smaller than in the older methods. This is especially important at the beginning of nitration, when the reaction is most vigorous.

4. Dangerous foaming often observed at the beginning of trinitration by the older methods is practically eliminated by the new method.

5. 'Burned' charges, often occurring in the older procedures and caused by a too rapid temperature rise during nitration, were not as numerous after the new method was introduced.

6. The new method is easier to operate and does not require such highly skilled workers as in the older methods. Because of increased production per line, labour requirements are much reduced.

7. The introduction of strong downward agitation and the use of undersurface toluene (or MNT) feed to the nitrating acid results in rapid and practically complete (except in trinitration) nitration during the time that the oil phase is below the surface of the acid in the nitrator. This type of 'bubble nitration' is particularly efficient when a strong downward agitation is used, and the time for the oil to rise to the surface is increased by the correct design of the organic substance feeder tube. In the old process, nitration occurred at the interface between the acid and oil layers – and delayed reactions ('sleeper charges'), excessive heats, etc., were rather common. At the same time improvement in uniformity of nitration was obtained, the improved agitation allowed better temperature control by more efficient distribution of the heat of reaction.

8. The advantage obtained by increased production and decreased cost of TNT was important.

It is interesting to note that the direct method of nitration was attempted in Europe as well as in the U.S.A. (Barksdale Plant), long before the Canadian and Keystone Ordnance Works trials indicated the great benefits derived from this process. However, the early European experimentation indicated that the method was unsafe and that it was difficult to control the important temperature and time factors. It seems highly probable that the difficulties encountered were due to improper feeding of toluene or MNT or DNT to the acid in the nitrator, poor agitation, inefficient cooling and the use of incorrect acid compositions.

Purification of Crude TNT

Three methods of crude TNT purification were in use in the U.S.A.:

(1) 'Soda-Ash' (sodium carbonate) process introduced by du Pont Co.,
(2) Ammoniacal 'Sellite' (ammonium–sodium sulphite) process introduced by the West Virginia Ordnance Works of General Chemical Co.,
(3) The alkaline 'Sellite' (sodium sulphite) process of Hercules Powder Co.

All three methods were designed to shorten the time of the operation and to reduce the quantity of water used. The latter requirement was dictated by the necessity to reduce the pollution of streams and water-ways with toxic sulphite solutions. To accomplish this completely the sulphite solutions were evaporated in a quadruple-effect evaporater to a thick syrup, the syrup was then fired in a rotary kiln incinerator to give an ash which was harmless to fish and animal life. The number of water washes of TNT was also reduced.

Soda-Ash Process

Crude 'Tri-oil' was washed with a small amount of hot water, followed by adding cold water to reduce the temperature in the wash-tank to 68°C. TNT solidified as fine crystals.

Sodium carbonate 20% solution was added to neutral (on litmus) reaction and care was taken to avoid an excess of alkali harmful to TNT. A solution of 16–17% NO_2SO_3 and 0.1–0.3% $NaHSO_3$ was added. The sodium–hydrogen sulphite was used to avoid alkaline reaction and also served as a buffer. Cold water was added to thicken the charge, the whole operation lasted 45 min. The product was screened through a 10 mesh sieve, centrifuged and washed with water. Larger particles were returned for reworking.

The washed TNT was dried (at 110°C) and flaked (Vol. I, p. 380, Figs 93, 94). The 'Flaker' is a steel drum rotating at constant speed and cooled on the inside by cold running water. By regulating the immersion of the drum in the molten TNT in the pan, the thickness of the solid product on the drum is controlled. A steel scraper removes the adhering TNT. It seems however (for safety purposes) preferable to use a bronze scraper as in the French method (Vol. I, p. 379).

Ammoniacal Sellite Process

This method is similar to the 'Soda-Ash' process. The difference consisted of using a solution of sodium sulphite (16–17% Na_2SO_3) added with ammonia gas by bubbling it to 2% free NH_3. The solution should have pH = 5. The pH value rose to 8.5 after mixing the solution with TNT (15 min). The solution contains: ammonium nitrate, sulphate and sulphite. Free sodium sulphite causes the formation of a red colour in the slurry of TNT with the aqueous solution. TNT made by this method is slightly darker owing to the action of ammonia on β- and γ-trinitrotoluene producing traces of 2,4- and 4,6-dinitro-3-toluidine. Traces of these impurities have not been found to adversely affect the quality of TNT.

The aqueous solution removed from TNT was not evaporated to incinerate owing to the presence of explosive ammonium nitrate in the solution.

Alkaline Sellite Method

Crude TNT is mixed with hot water and cold water is added to crystallize the product at 71°C. After washing to reduce the acidity to *ca.* 0.3% H_2SO_4, a calculated amount of Sellite solution was added containing 14.8–15.2% Na_2SO_3 and 1.1–1.6% Na_2CO_3. Mixing at 71°C lasted for 6 min after which the TNT was filtered. The washing, remelting, drying and flaking operations were carried out in the usual manner.

SAFETY OF MANUFACTURE AND HANDLING OF AROMATIC NITRO COMPOUNDS, PARTICULARLY OF BENZENE AND TOLUENE

(Vol. I, p. 391)

Although the number of accidents in the nitration of aromatic hydrocarbons is relatively small, the danger of the processes should not be underestimated.

As regards benzene and toluene the first and last steps of the reaction are particularly dangerous, i.e. the vigorous reaction of the hydrocarbon and the final nitration to introduce the second and third nitro group into benzene and toluene respectively.

An instructive description of a considerable number of accidents is given by Biasutti [76b].

In addition to those reported in Volume I, two accidents are described here.

In 1944 in a German factory which was built to the pattern of that of Krümmel (Vol. I, p. 357) an explosion took place during the nitration of benzene to nitrobenzene for the further nitration to dinitrobenzene. The reaction was carried out in a nitrator of 15 m^3 capacity. The nitrating mixture was added to benzene.

The explosion took place at the beginning of the reaction and demolished the building, although the nitrator suffered only slight damage. The conclusion of the investigation was that the explosion was produced by a gas mixture of benzene/air due to benzene leaking from the nitrator. This was probably the result of overheating the surface of the liquid in the nitrator. This in turn was the result of inadequate mixing produced by the incorrect design of the propellant stirrer (too small and too slow) and leaks from the nitrator which filled the building with explosive vapours of benzene/air.

The explosion took place through the discharge of static electricity.

As a result of the accident it was decided:

(1) to change the design of the stirrer to achieve better efficiency;

(2) to introduce nitrating mixture to the hydrocarbon,
(3) in both systems of adding acid to the hydrocarbon or vice versa it is advisable to introduce the acid and hydrocarbon respectively well below (0.5–1.0 m) the surface of the liquid in the nitrator. In this way, the hydrocarbon will be nitrated below the surface and its vapour pressure over the surface will be diminished.
(4) If acid is added to hydrocarbon a neutral gas (e.g. nitrogen) should be introduced into the nitrator to give a non-inflammable mixture over the surface of the liquid.

In another factory which used the same kind of nitrating system as in Krümmel, a major accident occurred in 1952. The whole building was destroyed together with several nitrators used solely for the nitration of DNT to TNT. Altogether *ca.* 80 tons of DNT/TNT exploded. The nitrators were at different stages of the process, in some of them the nitration proceeded at 95°C, in others with the stirrer stationary separation of the nitro compounds from the acid occurred. The accident began when a fire started in one of the nitrators where the separation of *ca.* 5 tons of TNT was in progress. The operators tried to quench the fire with a carbon dioxide fire extinguisher. This was unsuccessful and the whole team left the building. A fire-brigade arrived and at that moment the detonation occurred, 6 min after the fire started. A detailed examination of the cause of the fire and the detonation and an examination of analogous nitrators in other buildings lead to the conclusion that the fire was caused by drops of paraffin oil, which was used as a lubricant to impregnate asbestos washers tightening the axis of the stirrer. Laboratory experiments have shown that at a temperature of 95°C the vapours of nitric acid, containing of course nitrogen dioxide, can readily ignite paraffin oil present in a suspended string of asbestos. Burning gave a temperature of over 260°C which was sufficiently high to bring molten TNT (temperature – 95°C) to an explosive decomposition.

A few laboratory experiments have shown that fire in the nitrator–separator can be extinguished by resuming the work of the stirrer. This is due to a considerable amount of mixed acid which can act as a cooling and extinguishing liquid.

In a few instances disastrous effects have been produced by foreign bodies entering the nitrator or spent acid of trinitration. Such was the case of a rubber glove which had fallen into spent acid (Vol. I, p. 391) or rubber tubing which entered the nitrator (Radford, 1974) – according to [76].

In a factory a small explosion occurred when turning a stop-cock of the apparatus for sulphitation of molten TNT. It was found that deposits of picric acid or trinitrocresols and metal picrates (or trinitrocresates) were present in similar stop-cocks. An instruction was given that careful periodic cleaning of stop-cocks should be implemented.

The danger of keeping molten TNT at a high temperature has already been pointed out [45]. A heavy explosion of molten TNT transmitted to a store of 1700 kg of the same explosive occurred at Muiden, Holland in 1966 [76, 77]. It was estimated that the temperature of molten TNT in the melting tank was 150° or even 165°C. The melting tank was only used for remelting TNT refuse. Cardboard fibres were present in the molten TNT because of the dumping of faulty cartridges into the melt, and contaminants were able to accumulate in the tank. A similar accident with molten TNT occurred earlier (1940) at Bofors [76]. Molten TNT was contaminated with cardboard from cartridges of TNT. The cardboard was impregnated with linseed oil which floated on the surface of the melt. In the presence of air the oxidation of linseed oil could readily occur.

The last two accidents show the danger of contaminants on the behaviour of molten TNT.

The contamination of TNT with various organic substances such as lubricating oil, linseed oil, asphalt and varnishes lower its ignition temperature [78].

Also contamination of TNT with metals and their oxides can increase the danger of heating TNT (Vol. I, p. 392). It should be borne in mind that TNT is an acid which forms salts with metals, very sensitive to impact, friction and high temperature (Vol. I, p. 364). A patent [79] claims a practical use for TNT salts of Na, K, Cu (II), Ag (I), Ba, Pb (II), Fe (III), Al for delay compositions. Unwanted contamination of TNT with metals may lead to danger.

Although the nitration of aromatic compounds should be regarded as a relatively safe operation some unexpected decompositions and even explosions can occur due to some particular functional groups in the nitrated compounds. It is of course known that nitration of phenols by a direct reaction (Vol. I, p. 480) can bring about decomposition through oxidation. The same applies to *o*- and *p*-xylene (Vol. I, p. 395). Relatively recently attention was drawn to the danger of nitrating such an apparently 'harmless' compound as phthalic anhydride. The nitration to 3-nitrophthalic anhydride on a laboratory scale becomes very violent, after two hours with very little warning, the entire contents of the reactor were ejected [80]. This fact was rationalized in terms of the formation of phthaloyl nitrate, di-nitrate and – nitrite derivatives [81] – unstable substances which readily explode.

Häuptli [128] carried out extensive experiments on the influence of various 'foreign' substances on the decomposition temperature of TNT. Here are some of his results while adding 10% of a foreign substance:

pure TNT	297°C
with cork	257°C
dry 'red lead'	275°C
fresh red lead	192°C
linseed oil	220°C
asphalt	259°C

graphite	289°C
paraffin oil	260°C
mineral oil (lubricant)	249°C

L. C. Smith [129] pointed out that molten TNT can catch fire when mixed with activated charcoal (Norit). The mixture TNT (Norit 50) 50 begins to decompose at 110°C and at 174°C can produce an explosion.

Environmental Problems of TNT Manufacture (Vol. I, pp. 161, 389)

Two environmental problems are connected with TNT manufacture:

(1) poisoning of the atmosphere with tetranitromethane (TNT);
(2) the disposal of organic products formed during the sellite process.

The material balance shows that 0.4 ton of TNM and 4 tons of isomeric by-products are formed for 100 tons of TNT [98].

With regard to the recovery and use of TNM, its conversion into nitroform was suggested in the U.S.A. [98]. The known method of acting on TNM with aqueous alkali and hydrogen peroxide was recommended (Chapter VIII). Although the demand for nitroform exists and the method was economically justified, the application of the method was discarded as the quantity of nitroform obtainable was insufficient for potential requirements, and the requirement of the Environmental Protection Agency (EPA) can be satisfied by the destruction of TNM with sellite so that the substance will not be vented into the atmosphere.

With regard to solutions from the sellite process ('red waters') the problem of recovery of nitro compounds from the solution has already been discussed (p. 173). None of the suggested methods have received practical application and it appears that the best method of dealing with sellite wastes is evaporation to dryness and burning the residue as in Bofors-Chematur method [72].

Also the purification of TNT by crystallization from the acids (see also Vol. I, p. 378) should be considered. It offers the advantage that acids used for crystallization are recycled and enter the production process. However, the impurities present in the acid after crystallization are introduced into the nitrator which is a drawback of the method.

OTHER NITROAROMATICS

Nitro Derivatives of Hydrocarbons

In recent years very little attention has been given to nitro derivatives of higher homologues of benzene. Some of the homologues (e.g. xylenes) have become important starting substances in the production of valuable intermediates.

The only paper of any significance on the homologues of TNT was given by

Desseigne [119]. It referred to 2,4,6-trinitroethylbenzene (Vol. I, p. 414) which was obtained by a three-stage nitration of ethylbenzene. The yield was 77.7% and the setting point of the product 37° C.

Nitro Derivatives of Halogenohydrocarbons

Some halogenonitrohydrocarbons recently achieved importance as intermediates in the formation of important explosives. Such are: 1,3-dichloro- and 1,3,5-trichloro-2,4,6-trinitrobenzene which can serve to obtain high melting explosives: DATB and TATB (Chapter VII).

1,3-Dichlorobenzene can be commercially obtained by chlorination of *m*-dinitrobenzene (Vol. I, p. 193) and nitrated to the trinitroproduct which can be converted to DATB. A description of the industrial method of making 1,3,5-trichloro-3,4,6-trinitrobenzene was given in Vol. I, p. 469.

Nitrophenols (Vol. I, p. 492)

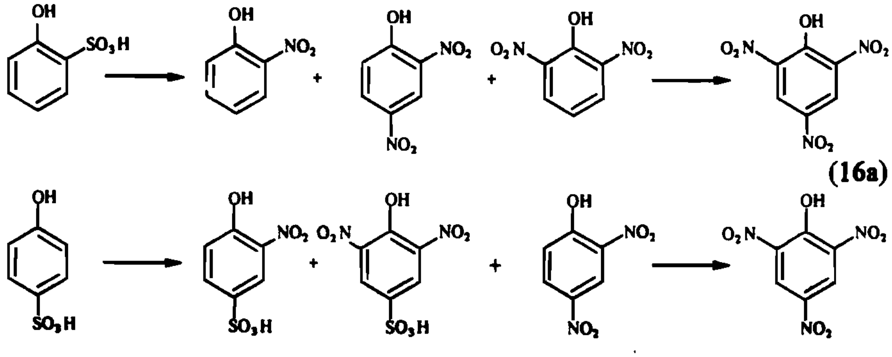
Relatively little attention is paid to high nitrated phenols as explosives, but some of them (e.g. styphnic acid) became important because of the initiating properties of their salts.

Picric Acid

Picric acid remains the best known highly nitrated phenol.

Some characteristics can be found in the monograph by Meyer [1] and attention was paid to chemical properties of picric acid and its substituted derivatives. Thus Pearce and Simkins [86] determined $\mathrm{p}K_a$ values (by calculation and experiment) of alkyl homologues of picric acid and its methoxy or halogen derivatives. The $\mathrm{p}K_a$ values fit well with data predicted from the Hammett relation. Styphnic acid however shows a deviation.

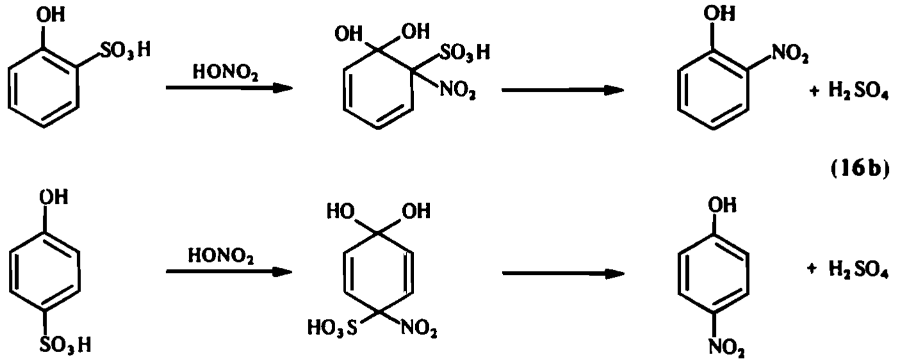
The mechanism of the substitution of sulphonic groups in phenol by nitro groups was extensively studied by Leśniak and T. Urbański [130] and to this purpose the chromato-polarographic method introduced by Kemula and associates [131] was used. The trend of the nitration of *o*- and *p*-phenolsulphonic acids with nitric acid can be depicted by diagram (16a):



(16a)

Thus the diagram on p. 501, Vol. I remains valid particularly as regards the nitration of *p*-phenolsulphonic acid.

The mechanism of the attack of nitric acid upon phenolsulphonic acids was rationalized by T. Urbański and Leśniak as passing through the addition stages forming transient yellow coloured quinoid structures (16b):



(16b)

Salts of Picric Acid

Salts of picric acid are important for two reasons:

(1) for their sensitivity to impact and friction which can be dangerous but can also be of practical importance in initiators and pyrotechnic compositions,
(2) they do not possess the undesirable property of picric acid, which is its acidity.

The salt in practical use is ammonium picrate. Its properties were described in Vol. I, p. 528. During World War II and explosive 'Picratol' composed of 52% ammonium picrate and 48% TNT was in use by the U.S. Army.

2,4-Dinitroresorcinol (Vol. I, p. 536)

A semi-industrial method of making 2,4-dinitroresorcinol was given by Ficheroulle and Soule [133]. It consists of two stages:

(1) Nitrosation
(2) Oxidation.

Nitrosation. The reactor was filled with 280 l. water and 6240 l. sulphuric acid (65.5 Be). 11,200 kg resorcinol were introduced and 100 kg of ice. A solution of 15 kg of sodium nitrite dissolved in 28 l. of water was added. Yellow coloured dinitroso compound was precipitated and immediately the solution was added to

480 g sodium sulphate in 2 l. of water. The precipitate was isolated by filtration, washed with cold water to neutrality (*ca.* 20 l.), finally it was dried and sieved with ethanol (2 l.).

The yield was 16 kg, i.e. 93.5%.

Oxidation. The reactor was filled with 45 l. of toluene and 10 kg of dinitrosoresorcinol. It was cooled to −5°C and over 8 hours 15 l. of nitric acid (d 1.35) diluted with 15 l. water were added. The product was filtered and washed three times with 30 l. water.

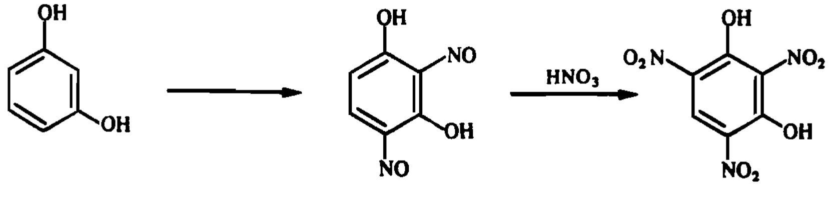
Purification

The dry dinitro compound was dissolved in 80 l. ether, the solution was filtered and ether distilled off. The product was dissolved by boiling with 140 l. water, then cooled and collected on a filter.

From 11,200 kg resorcinol 6500 kg dinitro product was obtained, i.e. the yield was 54–55%.

Styphnic Acid (Vol. I, p. 538)

Two papers [87, 88] have described a novel method of making styphnic acid. Both consist of two steps: (1) nitrosation of resorcinol to dinitroso derivative, (2) oxidation and nitration of the dinitroso compound (17):



(17)

The second step of the reaction can be carried out with nitric acid (d 1.40) at room temperature.

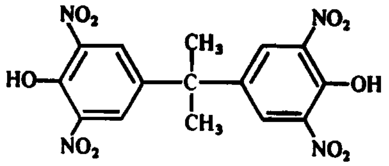
The advantage of this method as compared with the usual one of sulphonation and nitration is that in the usual method excessive foaming occurs.

The disadvantage of the new method is the fact that the dinitroso compound precipitates as a very fine powder, which is difficult to separate by filtration.

The properties of salts of styphnic acid will be given in the chapter dedicated to initiating explosives.

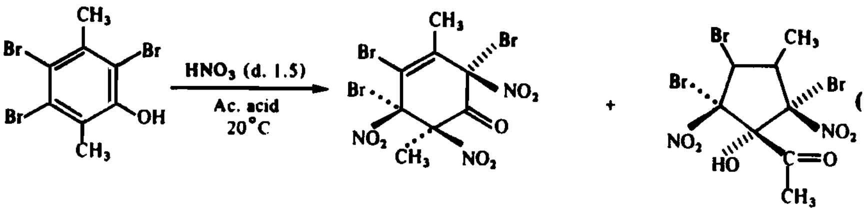
Tetranitrodian

2,6,2′,6′-Tetranitrodian was obtained by Szeky [89]. Its salts can be used as potential ingredients of pyrotechnic compositions.



IX m.p. 230-232°C

Nitro derivatives of a tribromophenol homologue. Zincke and Breitweiser [116] have found that dinitration of a tribromophenol homologue in the presence of acetic acid yielded two isomeric products. It was recently established (due to modern methods) [117] that nitration can also produce an interesting acyloin rearrangement leading to a five-member ring compound according to scheme (18):

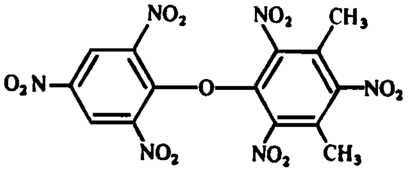


(18)

Picric Acid Ethers

Nitroanisols. Nitration of anisol to *o*- and *p*-nitroanisol was studied by Schofield and co-workers [90]. Mononitration in 54–82% sulphuric acid at 25°C gave the ratio $o/p = 1.8$–0.7.

Nitro derivatives of diphenyl ether (Vol. I, p. 549). Adamska and Okoń [91] prepared a number of methyl derivatives of penta- and hexadiphenyl ether, for example, 3,5-dimethyl-2,2',4,4',6,6'-hexanitrodiphenyl ether.



X m.p. 154-156°C

Nitro derivatives of aniline (Vol. I, p. 556). With the exception of hexanitrodiphenylamine nitro derivatives of aniline are not in use as explosives. Some of them are intermediates of reactions leading to highly nitrated compounds by oxidation $NH_2 \rightarrow NO_2$ according to the method of Nielsen, Coon *et al.* [10, 16]. See also [38].

Hexanitrodiphenylamine (Hexyl) (Vol. I, p. 562)

The data on explosive properties are also collected in the monograph by Meyer [1]. Some relatively new interest was created by salts of hexyl. They possess properties similar to those of picric acid: they burn readily and some of them show initiating properties.

Due to a very low solubility of its potassium salt, hexyl is used as a reagent for potassium. Also a suggestion was made for using hexyl to extract potassium from sea water [92]. The precipitated potassium salt treated with nitric acid yielded potassium nitrate which on evaporation crystallized out.

A considerable number of papers appeared by J. Hirst and co-workers [111] on the reactions of picryl chloride with substituted anilines. They studied the kinetics of the reaction and the influence of the substituents in aniline on Arrhenius parameters and rate constants.

Among other kinetic studies of picryl chloride and 1-chloro-2,4-dinitrobenzene with bases the works should be mentioned of Parker and Read [112] and Zollinger and co-workers [113] which have shown a much higher reactivity of picryl chloride. The reactions are greatly influenced by solvent and in some instances 1-chloro-2,4-dinitrobenzene is more reactive than picryl chloride [114].

The reactions belong to addition–elimination reactions AE $-S_N$ Ar [115].

Picramic Acid (Vol. I, p. 571)

A detailed description was given [93] for making picramic acid from picric acid and sodium hydrogen sulphide at 50–55°C with a yield of 88–90%.

Other Aromatic Nitro Compounds with Amino Groups

Some other aromatic nitro compounds such as DATB, TATB and DIPAM are of great practical importance and are described in Chapter VII (Heat Resistant Explosives).

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APPENDIX 1

DERIVATIVES OF HALOGENO-BENZENE

The nitro derivatives of chlorobenzene were described in Vol. I, pp. 450–471.

More recently nitro derivatives of fluorobenzene have received some attention. Olah, Kuhn and Flood [1] described the nitration of halogeno derivatives of benzene with NO_2^+ BF_4 (Made of N_2O_5, HF and BF_3) in tetramethylenesulphone as a solvent at 25°C and established different reactivities as compared with benzene (Table AI):

TABLE AI

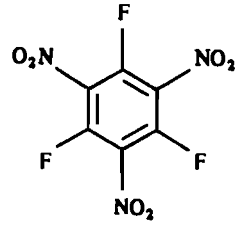
	Relative reactivity	Products % *o-*	*m-*	*p*
Benzene	1.0			
Fluorobenzene	0.45	8.5	–	91.5
Chlorobenzene	0.14	22.1	0.7	76.6
Bromobenzene	0.12	25.7	1.1	73.2
Iodobenzene	0.28	36.3	–	63.7

Also Kuhn and Olah [2] nitrated 2,4-dinitrofluorobenzene with NO_2^+ HSO_4^- in 100% sulphuric acid at 120°C for 12 hours and obtained picryl fluoride with the yield of 40%.

Fluorine in nitro derivatives of benzene shows a greater reactivity than chlorine in nucleophilic reactions [3]. In view of this attention was paid to 1,3,5-trifluorotrinitrobenzene and its reaction with nucleophiles [3].

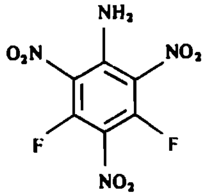
1,3,5-Trifluorotrinitrobenzene

An improved preparation was recently described [4]. High reactivity of fluorine excludes the displacement of nitro groups which was a side-reaction of analogous chloro- and bromo-nitro compounds.



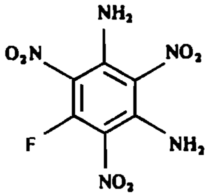
m.p. 80—82°C

By reacting 1,3,5-trifluorotrinitrobenzene with gaseous ammonia at −73°C the following compounds were obtained (I–III) by Adolph and co-workers [3]:



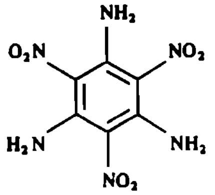
117 —118.5°C

I



m.p. 222—223°C

II

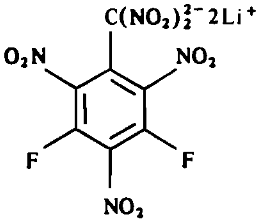


decomp

III

The yields of I, II and III were 42, 12 and 18% respectively.

Trifluorotrinitrobenzene reacted violently with hydrazine. Interesting was the reaction with lithium salt of dinitromethane resulting in formation of IV:



IV

A similar reaction with picryl chloride was described by Eremenko and co-workers [5].

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APPENDIX 2

ANALYSIS OF NITRATING ACIDS

Although analytical problems are outside the scope of the present book, it is advisable to mention the methods of rapid control of nitration. A considerable attention was recently paid to methods of acids analysis.

A brief description and references are given below. The novel methods are:

(1) Injection thermometry of Oehme and Ertl [1],
(2) Automation control of nitration by Belyaev, Kapustina and Peshekhonov [2],
(3) Redox titration of nitric acid in mixed acid [3] (see also Chapter 11).
(4) "In-line" analyser of nitric acid by:
  (a) refractometry
  (b) coulomb-polarography [4]
(5) High-frequency conductometric titration of mixed acid [5]
(6) Polarographic determination of nitric acid [6]
(7) By adding substances which can readily be nitrated by spent acid and the products of nitration can be quickly determined spectroscopically. One of the methods consists in adding salicylic acid which furnished two isomeric nitro compounds: 3- and 5-nitrosalicylic acid [7]. Their yield was determined by UV spectroscopy.

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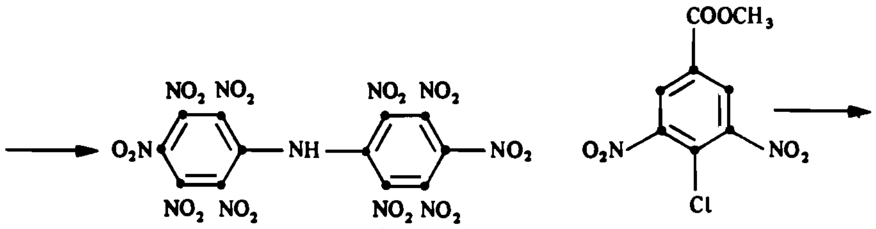
APPENDIX 3

Nielsen and co-workers described recently [1] the preparation of decanitrobiphenyl through a sequence of reactions starting from methyl ester of 4-chloro-3,5-dinitrobenzoic acid:



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CHAPTER 7

HEAT RESISTANT EXPLOSIVES

The last two decades have brought a new line of research in explosives. This is the work on heat resistant explosives.

There was an immense need in industry for an explosive composition which would be safe, reliable and stable at elevated temperatures. For example, it is sometimes necessary to shoot explosive devices in hot wells at temperatures which may reach as high as 200°–300°C. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperatures above 500°C. Using the explosives available at present, which have the best possible thermal properties, it is necessary to jacket the shaped charges with heavy insulation. Even so, the charge must be initiated within 3–4 min from the time it is set in place or it may fail due to thermal stability. There is also a growing demand in connection with space programmes for explosive compounds which are stable at elevated temperatures and low pressures. The explosive stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, which may raise the temperature of the filling above 80°C, so that the Torpexes (RDX/TNT/Al) and other conventional explosives are unsuitable for such stores.

Explosives with improved high temperature properties, usually called 'Heat Resistant Explosives' have emerged to meet such requirements. Nitro compounds have been found to be very useful heat resistant explosives. These compounds have received special attention and were reviewed by Dunstan [1], T. Urbański and Vasudeva [2]. They were of special interest [3–7] because of their ability to withstand the high temperatures and low pressures encountered in space applications. No doubt, the manufacture of these explosives is likely to be on kilogram rather than tonne scale, but the application is highly critical. Sometimes, even complex synthetic routes can be adopted, provided the product exhibits the requisite properties, a low vapour pressure and the ability to function satisfactorily after appropriate environmental trials, which may include heating at temperatures as high as 250°C. A few explosives that have these properties are listed in Table 1.

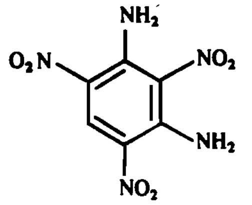
Bicyclic nitroaromatics, hexanitrostilbene (HNS) and diaminohexanitrodiphenyl (DIPAM) are in use for achieving stage separation in space rockets and for seismic experiments on the moon [7]. Single aromatic ring compounds, such as *m*-diaminotrinitrobenzene (TATB) have also been found to be of practical value in various space applications.

There has been speculation about the relationship between the exceptional thermal stability of these compounds and their molecular structure. Thermal decomposition studies show that the stability is associated with high melting point and low vapour pressure and there is evidence that the rates of decomposition are enhanced when substances are in liquid or vapour phase; they reach a higher energy level when molten or vapourized [8].

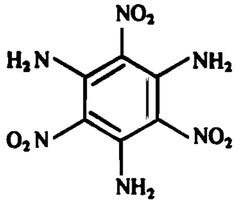
Solid state physical structure appears to be as significant as chemical constitution in determining the stability of explosives, but apart from crystal structure determination on lower molecular weight compounds, such as diaminotrinitrobenzene [9] there is little information available on the magnitude of molecular interactions or crystal lattice effects in these remarkable explosives.

NITRO DERIVATIVES OF BENZENE

1,3-Diamino-2,4,6-trinitrobenzene (DATB) (I) and 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) (II) have qualified as heat resistant explosives among the various nitro derivatives of benzene.

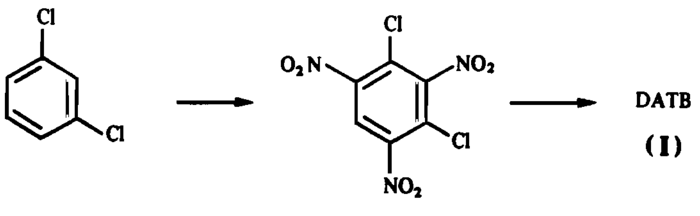


I



II

Several complicated procedures for the syntheses of diaminotrinitro benzene (DATB) have been reported. In one of these, the synthesis is accomplished [10–12] by vigorously nitrating *m*-dichlorobenzene at elevated temperatures. 1,3-Dichloro-2,4,6-trinitrobenzene thus obtained is aminated in methanol to yield DATB [13]. The yield has not been reported.

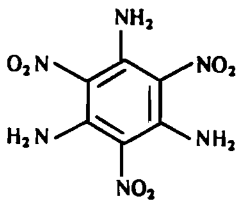


(1)

The second approach comprises the preparation of dipyridinium styphnate from styphnic acid in 94% yield. 1,3-Dichloro-2,4,6-trinitrobenzene can be obtained in 98% yield by allowing phosphorous trichloride and dipyridinium styphnate to react directly at steam-bath temperature. DATB was obtained by the amination reaction (mentioned above) in 97% yield. The overall yield of DATB (I) is considerably better than that obtainable by the existing procedures.

DATB is a lemon-yellow coloured crystalline substance. It is fairly stable when close to its melting point (286°C) decomposing at a rate of less than 1% per hour at 260°C, but it is transformed into crystal form of lower density at 216°C, which temperature, therefore, represents the limit of its utility. The use of DATB in highly explosive compositions has been described in several patents [14, 15].

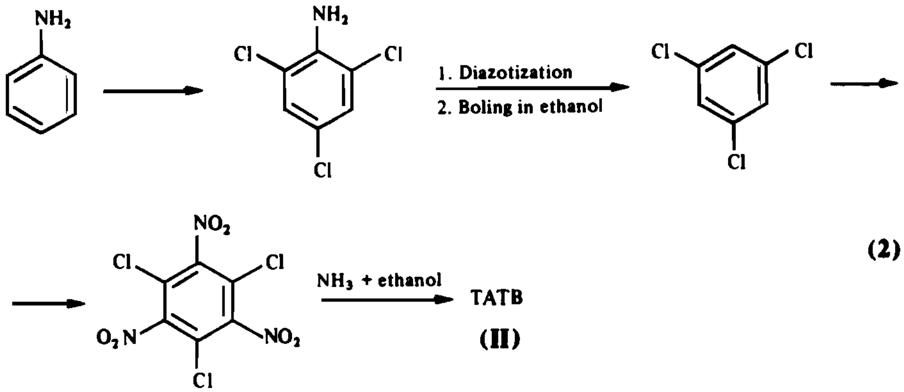
DATB forms charge–transfer complexes with aromatic hydrocarbons, aromatic amines, quinoline and iso-quinoline [37].



TATB

II

1,3,5-Trinitro-2,4,6-triaminobenzene (TATB) (II) was obtained in 1887 by Jackson and Wing [16] by the route shown in (2) which was substantiated later [16a].



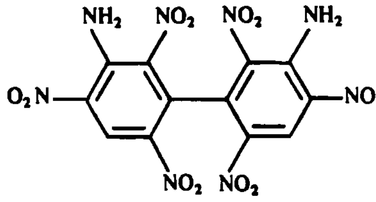
(2)

This is a yellow-brown coloured substance decomposing rapidly just below the m.p. (350°C) but it has excellent thermal stability in the range 260–290°C, which represents the upper temperature limit at which it may be used. The molecular structure of TATB was examined by X-ray analysis [44]. TATB possesses also a low sensitivity. However, the compressed or plastic bonded material tends to expand considerably. Subsequently Kolb and Rizzo [45] examined anisotropic thermal expansion between 214 and 377 K by X-ray analysis and found that the unit cell of TATB is formed by the planar sheets of the molecules whereas an amino group interacts with an *ortho* nitro group of the same benzene ring and with a nearest neighbour molecule. The sheets of TATB are bonded by strong intra- and intermolecular hydrogen bonds. A thermal volume change of 5.1% was found. Expansion was almost exclusively a function of a 4% increase in the axis perpendicular to the sheets of the molecules. The volume coefficient of thermal expansion for crystalline TATB was found to be $30.4 \times 10^{-5}\ K^{-1}$.

According to both groups of authors [44, 45] TATB is in triclinic form. Two other forms: another triclinic and monoclinic should be assigned to a polymorphic and impure substance respectively.

According to references in [45] a pilot plant for TATB exists in the U.S.A.

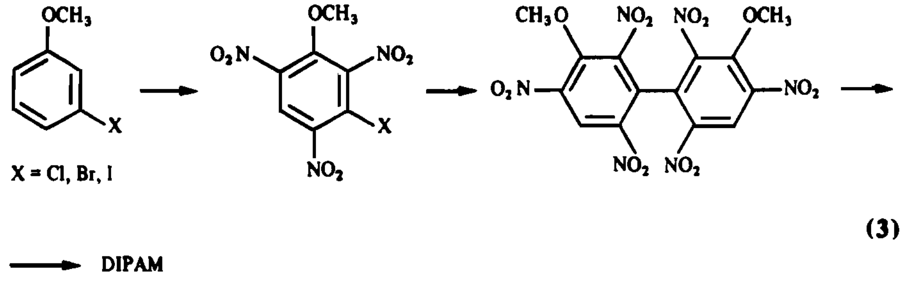
NITRO DERIVATIVES OF DIPHENYL



DIPAM

III

Among the nitro derivatives of diphenyl, 3,3-diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl (DIPAM) (III) has been found to be a thermally stable explosive. Oesterling and co-workers described a method in which the starting material is *m*-haloanisole. The reaction sequence is shown in (3).



(3)

DIPAM

(III)

The above method of preparing DIPAM comprises (a) nitration of a *m*-haloanisole with a mixture of nitric acid and oleum to obtain 3-halo-2,4,6-trinitro-anisole; (b) condensation of two molecules by reacting with a slurry of copper powder and a diluent to obtain 3,3′-dimethoxy-2,2′,4,4′,6,6′-hexanitrodiphenyl; and (c) amination to 3,3′-diamino-2,2′,4,4′6,6′-hexanitrodiphenyl (III) by introducing ammonia into a solution of hexanitro compound in a diluent which may be methanol, tetrahydrofuran or xylene–methanol–tetrahydrofuran mixture.

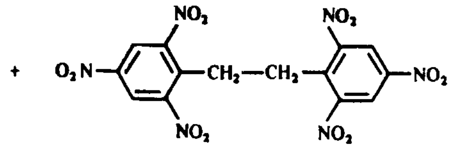
In addition to the ability of this explosive to withstand high temperatures, it is extremely insensitive to electrostatic discharge, requiring more than 32,000 J for initiation.

NITRO DERIVATIVES OF BIBENZYL AND STILBENE

Nitro derivatives of bibenzyl and stilbene are of considerable importance for two reasons: (i) some of them are produced by the nitration of toluene in the course of production of trinitrotoluene (TNT) as a result of the oxidation of CH_3 group; and (ii) some of them show very high melting points and can be regarded as classical examples of explosives resisting high temperatures.

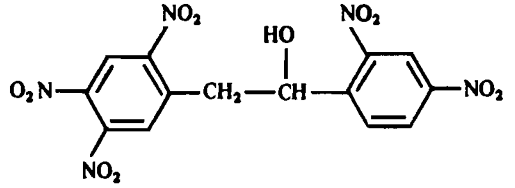
Nitro Derivatives of Bibenzyl

2,2′,4,4′,6,6′-Hexanitrobibenzyl (IV)



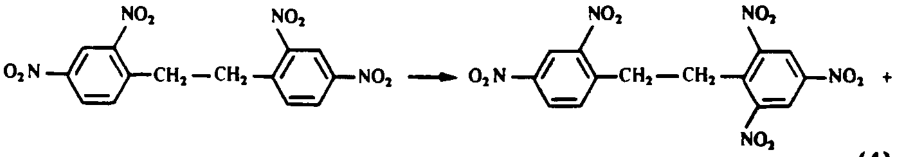
IV

This compound was obtained by Will [17] by nitrating 4,4′-dinitrobibenzyl. He also claimed to have obtained it by the alkaline oxidation of TNT. A substance of the same melting point was obtained by Rinkenbach and Aaronson [18] as a by-product of the nitration of 2,2′,4,4′-tetranitrobibenzyl by fuming sulphuric acid and fuming nitric acid at 85°C for a few days. The main product of nitration was claimed to be pentanitrodiphenyl ethanol: α-2,4,5-trinitrophenyl-β-2′,4′-dinitrophenyl hydroxyethane (m.p. 187°C) (V).



V

Blatt and Rytina [19] re-examined the findings of earlier workers. They nitrated bibenzyl and 4,4′-dinitrobibenzyl using 100% nitric acid and obtained 2,2′,4,4′-tetranitrobibenzyl (m.p. 171–172°C) with 90% yield of the crude product. The product could not be nitrated further unless it was subjected to vigorous nitration conditions, that is heating it with nitrating mixture composed of nitric acid (90% HNO_3) sulphuric acid (95% H_2SO_4) and oleum (15% SO_3) in a steam-bath for 7 hr, resulting in the formation of 2,2′,4,4′,6-pentanitrobibenzyl (m.p. 187–188°C) (VI) and a relatively small amount (*ca.* 10%) of hexanitrobibenzyl (IV), (4):



VI

(4)

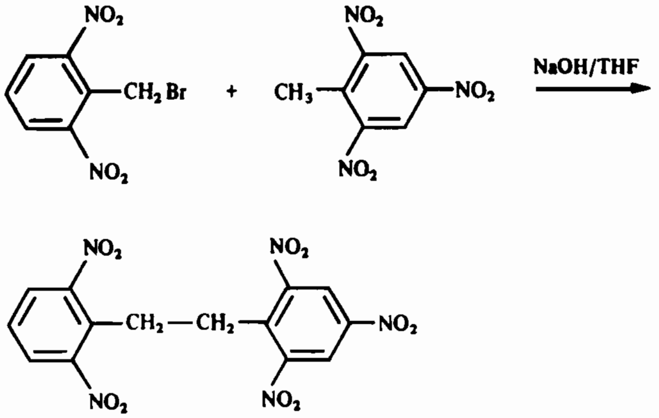
Nitration of pentanitrobibenzyl with the same nitrating mixture for 16 hr yielded 30% of hexanitrobibenzyl and unchanged pentanitrobibenzyl. Compound IV when crystallized from acetic acid, had m.p. 213–215°C. Shipp and L. A. Kaplan [20] nitrated bibenzyl using potassium nitrate in 30% oleum in the temperature range 60–120°C for 30 hr and obtained the product in 46.5% yield. After crystallization from hot acetone and water, IV melted at 218–220°C.

Neither Blatt and Rytina nor Rinkenbach and Aaronson were able to obtain hexanitrobibenzyl by the alkaline oxidation of 2,4,6-trinitrotoluene. However, this was achieved by Shipp and Kaplan [20] who found that TNT could be oxidized to hexanitrobibenzyl or hexanitrostilbene using sodium hypochlorite as the oxidizing agent. Thus, the observation of Will [17] proved to be correct. This was substantiated by Gilbert [51] who used methanol as a solvent at 50°C and a more concentrated hypochlorite solution, the yield was 82%.

Another process [20] consisted in reacting nitro derivatives of benzyl halogenides with trinitrotoluene in sodium hydroxide. In tetrahydrofuran 2,4,4′,6-tetranitrobibenzyl (m.p. 179–180°C) and 2,2′,4,6,6′-pentanitrobibenzyl (m.p. 155°C) were obtained (5).

Recently an Hungarian patent appeared [46] which consists in oxidative coupling of two moles of TNT in the presence of base, oxygen and a transition metal catalyst, for example, cobalt naphthenate at 50°C (in the presence of DMSO as a solvent) or cupric sulphate.

The method was examined by Golding and Hayes [47]. They tried to oxidize TNT in air in the presence of various catalysts, for example, anhydrous $CuSO_4$/pyridine in the presence of alcoholic KOH and triglyme. A high yield (55.5%) was obtained. Another high yield (53.4%) was given by Rodium (5% on alumin) in alcoholic KOH and triglyme.



(5)

The authors suggest a mechanism for the formation of the anion RCH_2^- [R = $(NO_2)_3C_6H_4CH_2^-$] which would react with the catalyst yielding a free radical according to (6):

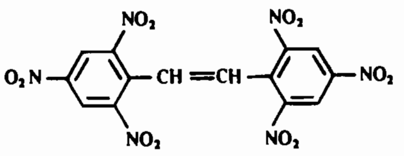
$$\begin{array}{lll} RCH_3 + OH^- \longrightarrow RCH_2^- + H_2O & (a) & \\ RCH_2^- + Co(II) \longrightarrow RCH_2^{\bullet} + Co(I) & (b) & \\ 2\,RCH_2^{\bullet} \longrightarrow RCH_2{-}CH_2R & (c) & (6) \\ Co(I) \xrightarrow{O_2} Co(II) & (d) & \end{array}$$

Oxygen (or air) regenerates divalent cobalt.

Also the radical ion reaction of the type given by Russell (Chapter IV) is possible.

Nitro Derivatives of Stilbene

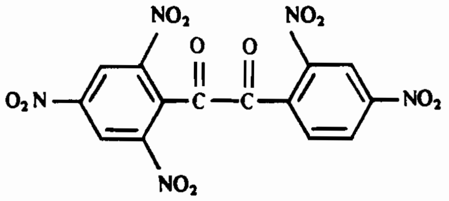
The most important nitro derivative of stilbene is hexanitrostilbene (HNS) (VII)



HNS

VII

The existing description in the older literature is not exact and requires new information. Very likely the product of m.p. 211°C described in Vol. I, p. 416 was not hexanitrostilbene but hexanitrobibenzyl. Also the direct nitration of stilbene does not furnish the required hexanitro derivative, as the double bond is highly vulnerable and oxidation can readily occur to form nitro derivatives of benzil: $C_6H_5CO.COC_6H_5$. Even nitro derivatives of stilbene on vigorous nitration furnish nitrated products of benzil. Thus Challenger and Clapham [21] nitrated 2,4,6-trinitrostilbene with a mixture of nitric acid (d 1.41) and sulphuric acid at 100°C for 2 hr and obtained 2,4,6,2′,4′-pentanitrostilbene (m.p. 198°C). When they applied a nitrating mixture composed of anhydrous nitric acid (d 1.5) and sulphuric acid at 100°C they obtained 2,4,6,2′,4′-pentanitrobenzil (VIII) (m.p. 260°C). Blatt and Rytina [19] nitrated 2,2′,4,4′-tetranitrostilbene by heating it with nitric acid (90% HNO_3), sulphuric acid (95%) and oleum (15% SO_3) in a steam-bath for 7 hr and obtained 2,2′,4,4′-tetranitrobenzil (m.p. 222°C).



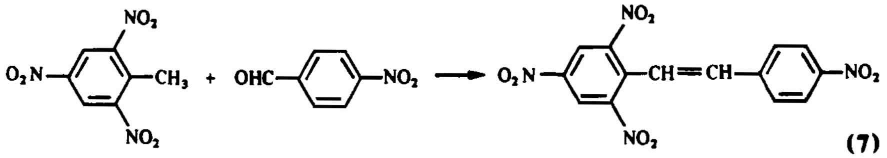
VIII

A few methods exist to produce nitro derivatives of stilbene. They are:

(1) reaction of nitro derivatives of toluene with benzaldehyde,
(2) reaction of nitro derivatives of benzyl halogenides with alkaline agents removing hydrogen halogenide,
(3) oxidation of nitro derivatives of toluene.

1. Reaction of nitro derivatives of toluene with benzaldehyde and its nitro derivatives. This type of reaction was first described by Thiele and Escales [22]. While heating a mixture of 2,4-dinitrotoluene with nitrobenzaldehyde at 160–170°C and allowing the reaction mixture to rest for 2 hr, they obtained all the three possible isomers of 2,4,4′-trinitrostilbene using *o*-, *m*- and *p*-nitrobenzaldehyde.

In a similar way, Ullman and Geschwind [23] obtained 2,4,6,4′-tetranitrostilbene (m.p. 196°C) from trinitrotoluene and *p*-nitrobenzaldehyde.

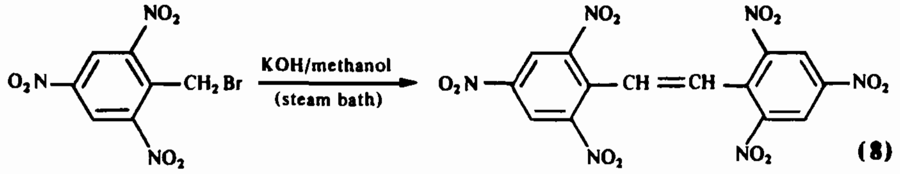


(7)

Shipp [24] tried the same reaction between trinitrotoluene and trinitrobenzaldehyde and obtained hexanitrostilbene in poor yield.

2. Preparation from nitrobenzyl halogenides. This method consists in reacting nitrobenzyl halogenides with alcoholic potassium hydroxide. The reaction was described for the first time by Krassusky [25] who obtained 2,4,2′,4′-tetranitrobenzyl (m.p. 266–267°C) by warming 2,4-dinitrobenzyl chloride with potassium hydroxide in ethanol. The reaction did not seem to be successful when 2,4,6-trinitrobenzyl bromide was used as the starting material contrary to the finding of Reich and co-workers (Vol. I, p. 416).

Shipp [24] obtained 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) in 30% yield by reacting 2,4,6-trinitrobenzyl halogenide with alcoholic potassium hydroxide (8). The product melted at 316°C,



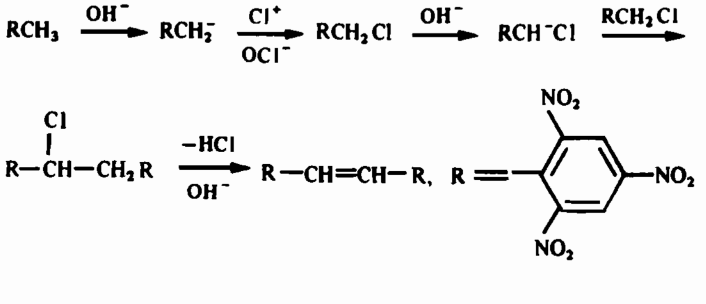
(8)

VII

that is, 105°C above the melting point of the product obtained by Reich. The correct structure of the compound follows from the synthetic route given by Shipp [24].

3. Preparation by oxidation of nitro derivatives of toluene. A number of methods involving this approach have been developed. They can lead to derivatives of both bibenzyl and stilbene. Thus, Green and co-workers [26] obtained 4,4-dinitrobenzyl (m.p. 180–182°C) by oxidizing *p*-nitrotoluene with air in potassium hydroxide solution in methanol at room temperature. When the reaction mixture was warmed 4,4-dinitrostilbene resulted. Green and Baddiley [27] reacted 2,4-dinitrotoluene with diiodine in the presence of pyridine in potassium hydroxide solution in methanol at 40–50°C and obtained 2,2′,4,4′-tetranitrostilbene (m.p. 266–267°C).

Shipp and Kaplan [20] obtained 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) by oxidizing TNT with sodium hydrochlorite. The method consists in adding 10 parts of 5% sodium hypochlorite solution to a chilled solution of 1 part of TNT in 10 parts of methanol. The solution is allowed to stand at ambient temperature until HNS precipitates as a fine crystalline product. The product is crystallized from nitrobenzene to yield pale yellow coloured needles. The mechanism of the reaction is shown in reactions (9).



(9)

It is possible to isolate 2,4,6-trinitrobenzyl chloride or the bimolecular product α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl by stopping the reaction short. This is indeed an excellent preparative reaction for the chloride replacing the tedious series of reactions which had been the only known route for this compound [28].

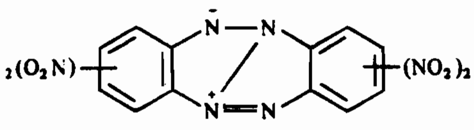
HNS can form charge–transfer complexes with a number of aromatic amines and phenols [38].

A novel method of producing nitrostilbene derivatives was given by Bethel and Bird [48]. It consists in reacting 4-nitrobenzylhalides with potassium *t*-butoxide. 4,4-Dinitrostilbene resulted.

According to [47] full scale production of HNS exists in the United Kingdom based on the method of Shipp [24].

NITRO DERIVATIVES OF AROMATIC AZA PENTALENES

Tetranitro derivatives of dibenzo-1,3a,4,6a-tetrazapentalene (TACOT) (IX):



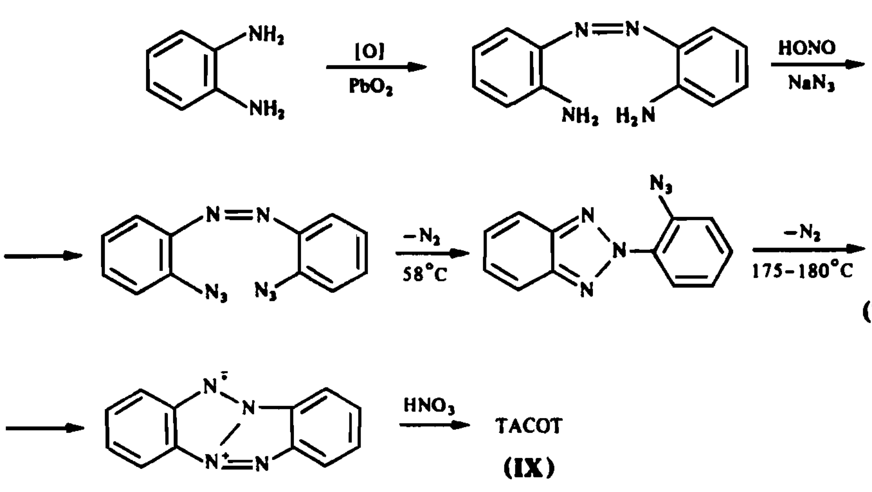
TACOT

IX

This is a mixture of isomers with two nitro groups substituted in different positions in each benzene ring. It is a powerful explosive with unusual and outstandingly high temperature stability [29] TACOT, which is comparable to pentaerhythritol tetranitrate (PETN) in explosive power, has thermal stability greater than that reported for any known organic explosive compound or composition.

TACOT was described for the first time in 1960 in a patent [30] and later in many papers by Carboni and co-workers [31–36] in which the syntheses of this compound and its properties were reported. It can be obtained from *o*-phenylenediamine by the sequence of reactions (10).

Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene is generally prepared from tetraazapentalene by direct nitration. The procedure [29] consists in adding 30 parts of fuming nitric acid to 1 part of dibenzo-1,3a,4,6a-tetraazapentalene in concentrated sulphuric acid. After 15 min, the mixture is heated to 60°C and maintained at this temperature for an additional 15 min period. The orange coloured mixture is poured into ice-water to yield TACOT, which can be recrystallized from dimethyl formamide. The product obtained is composed of numerous isomers of tetranitrodibenzo-1,3a,4,6a-tetraazapentalene, depending on the position of the nitro group (*ortho, meta* or *para*) in each individual



(10)

(IX)

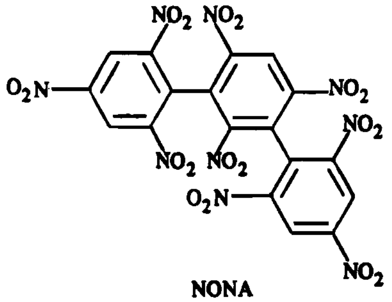
benzene ring. But these isomers have been found to have similar explosive and thermal properties. Therefore TACOT which is a mixture of the three isomers, is used as such in explosive compositions. Its ignition temperature (494°C) is the highest ever registered for explosives. Its explosive power is equal to 96% and 80–85% that of TNT and RDX respectively. It is highly insensitive to impact and compares favourably with dinitrobenzene in that respect. Despite the insensitivity to impact and static charges TACOT can be readily initiated by lead azide primer containing as little as 0.02–0.03 g of lead azide.

TABLE 41. Heat resistant explosives

Explosive	Chemical name	m.p. °C	Crystal density g/cm^3	Velocity of detonation m/sec	Detonation pressure (calc.) k bars
DATB	1,3-Diamino-2,4,6-trinitrobenzene	286	1.84	7500	260
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene	350 (decomp.)	1.94	7500	290
HNS	2,2′,4,4′,6,6′-Hexanitrostilbene	318	1.74	7000	215
DIPAM	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	304	1.79		
TACOT	Tetranitro-2,3: 5,6-dibenzo-1,3a,4,6a-tetra-azapentalene	410	1.85	7200	245

NONA

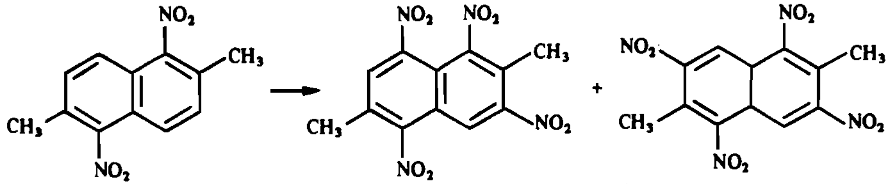
NONA is 2,2′,2″,4,4′,4″,6,6′,6″ – nonaterphenyl obtained by reacting 2 moles of picryl chloride with 1,3-dichloro-2,4,6-trinitrobenzene in the presence of copper dust at 210°C (Ullman reaction) [55]. It has an exceptional heat stability melting with decomposition at 440–450°C. It has a density of 1.78. No more information is available.



NONA

POTENTIAL HEAT RESISTANT EXPLOSIVES

Some work has been done to obtain new heat resistant explosives. A number of potential products were thus obtained, Buckley, Everard and Wells [39]. They nitrated 2,6-dimethyl-1,3-dinitronaphthalene [40] using nitric acid in acetic anhydride and obtained tetranitro derivatives marked by their high melting points in addition to a small amount of a trinitro compound not shown on formula (11).



(11)

It was suggested that the above compounds should be used to produce analogues to hexanitrostilbene by their oxidation.

Buckley and co-workers [56] continued their work on high nitrated naphthalene derivatives. They nitrated 1-methylnaphthalene with dilute nitric acid (d 1.42) in Cl CH_2CH_2Cl at 40°C and obtained 4,8- and 4,5-dinitro-1-methylnaphthalene (I and II respectively).

On further nitration below 2°C with nitric acid (d 1.5) and sulphuric acid (d 1.84) they obtained trinitro- and tetranitro derivatives, of relatively low melting points:

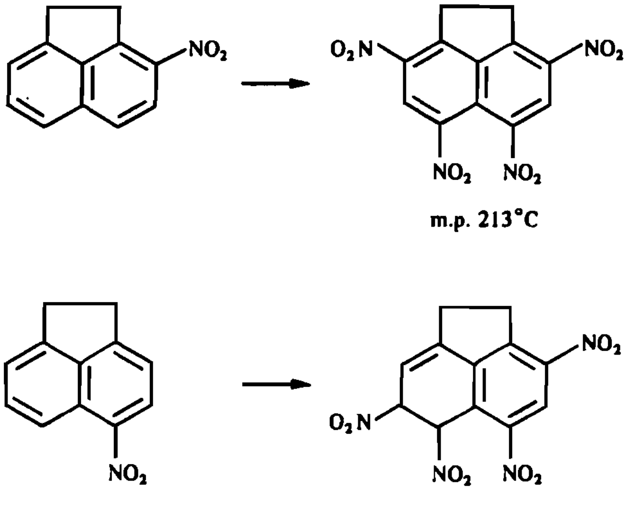
I ⟶ 2,4,8-trinitro-, 4,5,8-trinitro- and 2,4,5,8-tetranitro-1-methyl naphthalene
m.p. 135–138°C m.p. 218°d m.p. 220°C

II ⟶ 2,4,5-trinitro-1-methyl naphthalene (m.p. 190°d)

The yields of tetranitro derivatives were low (6%).

Another line of research consisted in producing polynitroacenaphthene [41]: 3-, 4- and 5-nitroacenaphthene were nitrated and yielded di, tri- and tetranitroacenaphthenes. Also pentanitroacenaphthene was obtained. None of the substances has shown a very high m.p., the highest was that of 3,7-dinitroacenaphthene (m.p. 276°C).

However, tetranitro derivatives obtained by nitration of 3- and 4-nitroacenaphthenes, 3,5,6,8- and 3,5,6,7-tetranitroacenaphthenes (12a) and (12b) respectively can be of some interest as explosives.



(a)

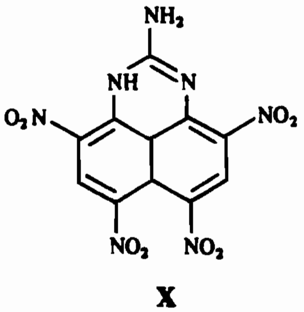
(12)

(b)

m.p. 157°C

Another potential heat resistant nitro compound is 2-amino-4,6,7,9-tetranitroperimidine (X) [42]. The mother substance: 2-aminoperimidine can be obtained from perinaphthylene diamine and ammonium cyanate with a good yield [43]. The substance is used in analytical chemistry as a reagent for sulphate ion because of the very low solubility of the sulphate.

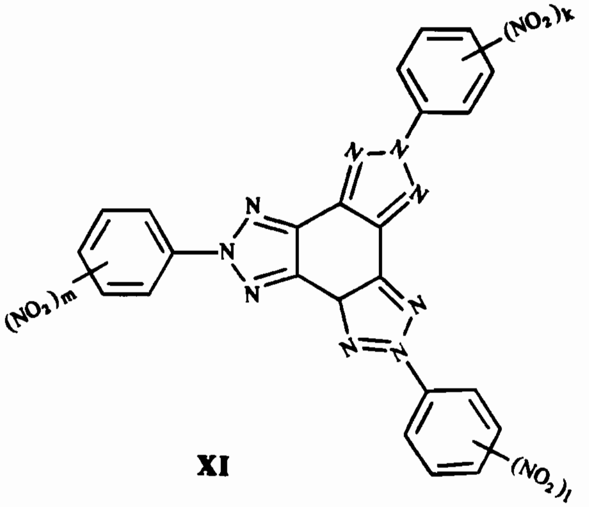
It was recently announced [50] that 1,3,5,7-tetranitroadamantane (TNA) possesses properties which are likely to be of value as a heat resistant explosive. Its m.p. is above 350°C. It is also very insensitive to impact.



X

In some countries Octogene (HMX) is considered as a heat resistant explosive [50, 51]. Its m.p. was found to be between 276–277°C (Vol. III, p. 117) and 280°C [51].

Nitro derivatives of 2,5,8-triphenyl-tris-triazolobenzene (XI) are very interesting heat resistant compounds [52]. The substances were obtained by coupling diazotized nitroanilines with 1,3,5-triaminobenzene, followed by oxidation with $CuSO_4$. Compounds from *p*-nitroaniline and 2,4-dinitroaniline had m.ps of 369–370°C and 400°C respectively.



XI

Resistance to Irradiation

The heat resistant explosives: TACOT, DATB and TATB are remarkably stable towards various irradiations such as gamma radiation from Co^{60} according to Avrami [49].

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APPENDIX

Kuboszek and co-workers used phase-transfer catalysis and catalytic two phase system to obtain some heat resistant explosives such as: HNS [1, 2], HNBB [3], Hexanitrodiphenylmethane [4], Hexanitrodiphenylamine [5] and polynitro derivatives of polyphenylethers [6].

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CHAPTER 8

ALIPHATIC NITRO COMPOUNDS

(Vol. I, p. 579)

In the course of the last two decades the chemistry of aliphatic nitro compounds – both nitroalkanes and nitroalkenes has received particular attention. A variety of compounds have been obtained and their properties examined.

Between 1950 and 1960 increased interest in the use of nitroalkanes as potential explosives and propellants has been a major factor in expanding the chemistry of this relatively ignored field.

Evidence of the increasing interest in the field were Symposia on Nitro Aliphatic Chemistry in 1961 [1] on Nitro Compounds in 1963 [2], and in 1968 [3]. Then a few excellent review articles appeared by: Doležel [4], Noble, Borgardt and Reed [5], Shechter [6a], Shechter and R. B. Kaplan [6b], a review on nucleophilic substitution $S_{RN}1$ of aliphatic nitro compounds by Beletskaya and Drozd [245], collective volumes edited by H. Feuer [7], monographs by: Perekalin and Sopova [8], Novikov and co-workers [9]. See also [120]. Some books exist where the chemistry of nitroalkanes form important chapters, viz.: by Asinger [10], Matasă and Matasă [11], Sosnovsky [12].

Nitroalkanes have also opened some new fields in organic synthesis. The problems were tackled in a number of monographs and review articles [13–19] – however, most of them are outside the scope of the present book. Such is also the monograph by Krein and Shekhter [233] describing the nitration of lubricating oils to produce anti-corrosion materials.

There are some natural nitroalkane derivatives existing, such as β-nitropropionic acid present in some plants.

MONONITRO ALKANES

As is known (Vol. I), alkanes can be nitrated in vapour phase by nitric acid or nitrogen dioxide. Nitration with nitric acid at temperatures of 400–435°C (method of Hass, Vol. I, p. 86) became a well established commercial method of making nitroalkanes. A considerable number of papers mainly by Hass and coworkers (Vol. I) and Titov (Vol. I) gave both theoretical and practical foundations for this remarkable process and subsequently less theoretical work has appeared. Less attention was paid to the nitration of alkanes with nitrogen dioxide (method of T. Urbański and Słoń, Vol. I, p. 94) which has not been put to industrial use.

The author of this book continued some of his work, for example, nitrating *n*-heptane with a great excess of nitrogen dioxide [20]. It was found that equal distribution of the nitro groups occurred along the chain: *ca.* 40% were found for positions 2 and 6, 3 and 5, and *ca.* 20% for position 4. This confirmed the view expressed by Hass (Vol. I, p. 95) and Asinger (Vol. I, p. 95), [10, 21, 22] that the nitration of CH_2 groups of longer chain alkanes proceeds according to the statistical rule. This finding was contrary to some views that position 2 in long chain alkanes is the preferred position [23].

Ślebodziński, T. Urbański and Łukasiewicz [24] nitrated *n*-hexane with nitrogen dioxide at temperatures varying from 120° to 300°C with molar ratios *n*-hexane:NO_2 varying from 1:10 to 5:1. The highest yield and safest conditions were obtained with the ratio 3:1 at 300°C. The yield of nitro compounds was *ca.* 42% in relation to *n*-hexane converted. The composition of the nitro alkane fraction was as given in Vol. I, pp. 94–95.

The identification of nitroalkanes was carried out by coupling nitroalkanes with diazonium salts [25]. The method was based on the work of V. Meyer *et al.* [26] and used by some authors for the identification of nitroalkanes [27, 28].

With the advent of chromatography the method of gas chromatography was used for the separation and identification of nitroalkanes. This was described in papers by Bethea and Wheelcock [29]. The gas–liquid chromatography of C_1-C_4 nitroalkanes was used by Biernacki and T. Urbański [30].

Minc, T. Urbański and Falęcki [96] examined the action of ionizing radiation from Cobalt source (Gamma Cell 220) upon *n*-hexane dissolved in N_2O_4 in sealed tubes. The reaction was carried out for 200 hr at room temperatures, and the yield of 1-nitrohexane was 1%. The experiments were discontinued when a violent explosion occurred in one of the tubes.

Albright *et al.* [97] examined the influence of gamma radiation upon the vapour phase nitration of propane with nitric acid at 400–450°C. There was a slight effect of irradiation on the yield of nitro products, in agreement with the above finding [96]. The increase of the yield of nitro alkanes was of the order of only 10–15%.

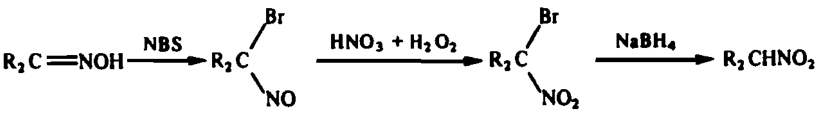
OTHER METHODS OF INTRODUCING THE NITRO GROUP INTO SATURATED COMPOUNDS

The other methods of introducing the nitro group into saturated compounds have been reviewed by Larson [31].

Here are the main outlines for the conversion of oximes to nitro compounds.

Emmons and Pagano [32] used peroxytrifluoroacetic acid to oxidize oximes to nitro compounds with a yield of up to 76%. The reaction is carried out in acetonitrile as a solvent in the presence of a buffer to neutralize trifluoroacetic acid formed in the reaction. This is a simple and convenient method of obtaining nitro aliphatic and alicyclic compounds. Thus, nitrocyclohexane and 1-nitroheptane were obtained with yields of 62 and 72% respectively. See also [33].

Another method of oxidation of ketoximes to nitro compounds consists in the bromination of ketoximes with *N*-bromosuccinimide to obtain bromonitroso compounds which were oxidized with nitric acid and hydrogen peroxide to bromonitro compounds. The latter were debrominated by sodium borohydride to yield secondary nitro compounds [34] (1):



$$R_2C{=}NOH \xrightarrow{NBS} R_2C(Br)(NO) \xrightarrow{HNO_3 + H_2O_2} R_2C(Br)(NO_2) \xrightarrow{NaBH_4} R_2CHNO_2$$

(1)

The method has found an application to the preparation of nitro steroids [35].

Oximes can be oxidized to nitro compounds with ozone [227], and recently an excellent yield was obtained by oxidation of ketoximes with hypochlorous acid to form chloronitroso compounds which on further oxidation with tetra-*n*-butylammonium hypochlorite yielded secondary nitroalkanes [228].

Oxidation of Amines

The reaction of the oxidation of aromatic amines to nitro compounds examined by Emmons and co-workers (Vol. I, p. 132) gave a high yield of nitro derivatives. Emmons [36] tried to use peracetic acid to obtain tertiary nitroalkanes. The reaction gave a high yield (e.g. nitrooctane was obtained with a yield as high as 87%). The use of peroxytrifluoroacetic acid, successful in the oxidation of oximes, did not give favourable results with amines. To obtain nitrosteroids from the amines, *m*-chloroperbenzoic acid was successfully used (the yield was 50–79%) [37].

Potassium permanganate can also be used to oxidize tertiary amines otherwise resistant to oxidation [38].

Reaction of Alkyl Halides with Sodium Nitrite

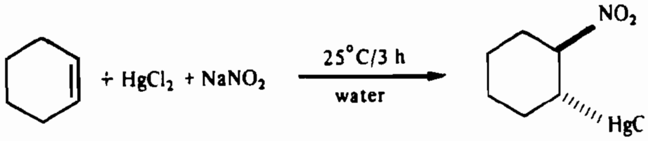
The method of Kornblum (Vol. I, p. 127) received a wide application, for example, for the synthesis of α-nitro esters [39] and β-nitroketones [40]. However, this method has some limitations. Thus *t*-butyl halide does not furnish the expected nitro compounds. Also cyclohexyl bromide does not react with sodium nitrite. On the contrary, cyclohexyl iodide reacts with sodium nitrite but the product is cyclohexane in 57% yield.

Similar to the reaction of V. Meyer, nitrous esters are also formed during the

Kornblum reaction, for example, bromocyclopentane is converted to both nitro cyclopentane and nitrous ester [41]. For more information see [31].

Nitromercuration of Alkenes

An interesting reaction of nitromercuration was found by Bachman and Whitehouse [107]. It consists in acting with sodium nitrite and mercuric chloride on alkenes, for example, on cyclohexene (2):



(2)

β-Nitromercurial chloride results with the yield of 80%. The products were used to obtain nitroalkenes (28a).

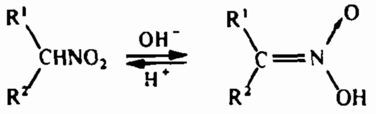
Formation of Nitroalkanes from Nitrate Esters

Thermal decomposition of nitrate esters has been shown to result in the formation of small amounts of nitroalkanes [237]. Bachman and Connon [238] described the method of converting nitrate esters into nitroalkanes by reacting nitrate esters with metal nitrites in suitable solvents. More detailed information is given in Chapter X on nitrate esters.

CHEMICAL PROPERTIES OF NITROALKANES

Nitronic Acids

One of the most important properties of primary and secondary nitro alkanes is their ability to form aci-nitro compounds, also referred to as nitronic acids:

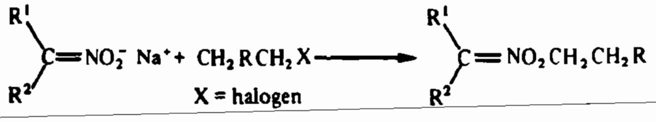


(3)

Polar Solvents Favour the Aci-form

Nitronic acids are relatively weak ($pK_a = 2–6$) resembling carboxylic acids with regard to their strength. The nitronic acids can form esters. They can be prepared in three ways:

(1) by the alkylation of sodium or potassium nitronate salts, for example,



(4)

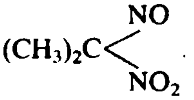
(2) by the alkylation of silver nitronate salts,
(3) by the reaction of nitro alkenes and nitronic acids with diazomethane.

Method (1) has considerable limitations, as the nitronic ester decomposes readily to yield oximes and aldehydes and ketones.

Nitronic esters are able to enter the 1,3-addition reaction (Chapter IV, formula 30).

Armand *et al.* [261] described reactions of nitronic acids. They found that by acidifying ion nitronate $(CH_3)_2C = NO_2^-$ a number of compounds can be formed depending on pH. Thus under pH = 5 and 3 the main products are: the same nitroalkane of 85% and 6% yield respectively.

At pH = 3 the main product (31%) was nitro-nitroso compound



$$(CH_3)_2C{<}\begin{matrix}NO\\NO_2\end{matrix}.$$

Salts of nitronic acid can decompose readily in a dangerous manner. Particularly dangerous are salts of nitromethane (Vol. I, p. 586; Vol. III, p. 136). Dry sodium salt of nitromethane can explode when touched with a spatula.

The chemistry of nitronic acid and derivatives is a very wide field and the reader should consult an excellent monographic review by Nielsen [42].

Activating Influence of the Nitro Group

The nitro group activates aliphatic systems and makes possible a number of addition reactions such as: aldolic addition of aldehydes (Henry reaction), Mannich reaction, Michael addition, Diels–Alder reaction, for example [155].

The reader should be advised to consult an excellent monographic review given by Baer and Urbas [43].

Here are a few data based on more recent publications.

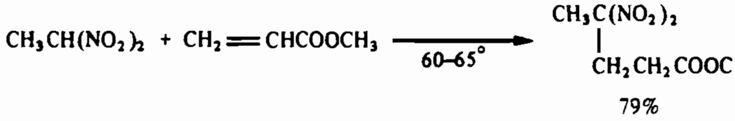
1. Aldolic addition and the Mannich reaction (Vol. I, p. 186). The aldolic addition reaction of nitroalkanes with carbohydrates (specifically aldoses) continues to be an important reaction in sugar chemistry which according to Baer [43] in some respects surpasses in versatility Emil Fischer's classical cyanohydrin synthesis. Particularly noteworthy are publications by Baer and Kovář [44, 45], Funubaski, Yoshimura and co-workers [46–51] and other Japanese workers [52], Russian workers [53, 54] and Bilik [55].

A different method of preparing glucosinolates through nitroalkanes was given by MacLeod and Gil [56].

With regard to the Mannich reaction the monographs, for example, that of Reichert [57] should be consulted.

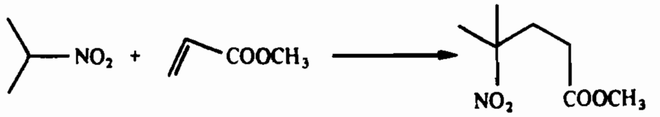
2. Michael addition. Ostaszyński and Wielgat [58] used potassium fluoride as a catalyst for the Michael addition of nitromethane to a double bond. (Alkali fluorides were originally suggested by Yasuda *et al.* [59] as catalysts for the

Michael addition reactions.) The work of addition of nitroalkanes was continued [60]. Various acceptors, for example, methylacrylate and acrylonitrile, were used. Among nitroalkanes gem-dinitroalkanes were applied as donors. Nitroalkanes readily formed double salts with KHF_2, $RbHF_2$ and $CsHF_2$. The yield of the adducts of such salts with compounds containing a double bond varied between 60 and 90%, viz. (5):



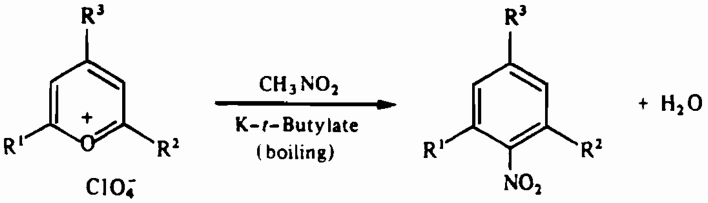
$$CH_3CH(NO_2)_2 + CH_2{=}CHCOOCH_3 \xrightarrow[60\text{–}65^\circ]{} \underset{79\%}{\begin{array}{c}CH_3C(NO_2)_2\\ |\\ CH_2CH_2COOCH_3\end{array}} \qquad (5)$$

Alternatively, nitroalkanes can be added to an activated double bond, (6) [61]:



(6)

3. ***Reaction of nitromethane with pyrilium salts.*** Dimroth [62] in a number of papers since 1956 [63] has described an interesting reaction in the formation of aromatic nitrocompounds by reacting nitromethane with pyrilium salts (e.g. perchlorate) substituted in positions 2,4,6 in basic medium (7) with a yield varying from 25 to 60%:

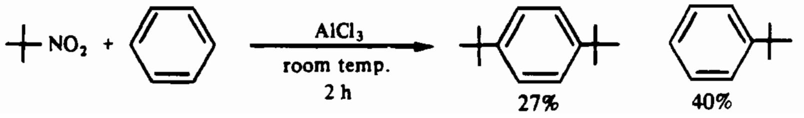


(7)

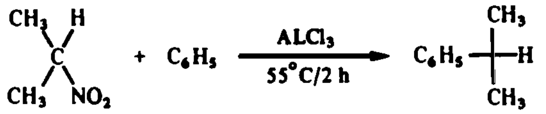
By-products of the reaction are cyclohexylinden derivatives.

4. ***Nitroalkanes as alkylating agents in Friedel-Crafts reactions.*** An interesting reaction was recently reported by Casini and co-workers [64]. They found that Friedel-Crafts reaction of benzylic or tertiary nitro compounds with benzene gave normal alkylation products (8) and (9) respectively. 2-Nitropropane gave cumene (10) subject to further transformations.

$$C_6H_5CH_2NO_2 + C_6H_6 \xrightarrow[\text{room temp.}\ 24\ \text{h}]{AlCl_3} \underset{10\%}{C_6H_5CH_2C_6H_5} \qquad (8)$$



(9)



$$(CH_3)_2CHNO_2 + C_6H_5 \xrightarrow[55°C/2\,h]{AlCl_3} C_6H_5C(CH_3)_2H \qquad (10)$$

5. ***Oxidation of nitroalkanes to aldehydes and ketones*** (Vol. I, p. 186). The Nef reaction (Vol. I, p. 186) for the formation of aldehydes and ketones from primary and secondary aliphatic nitro compounds was modified by Nametkin and Pozdnyakowa [90] and Grundman [91] who improved the yield of ketones (from secondary nitroalkanes) by using an oxidizing medium of potassium permanganate and hydrogen peroxide respectively. The reaction with permanganate was extensively used by Asinger *et al.* [20b, 22], Ślebodziński, T. Urbański *et al.* [24] in the analysis of the products of nitration of long chain alkanes.

McMurrey and co-workers modified the reaction by carrying it out in a reductive medium of $TiCl_3$ followed by hydrolysis and an oxidizing medium of O_3 [92a] and [92b] respectively. See also Bartlett *et al.* [93]. They used *t*-butyl hydroperoxide in the presence of pentavalent vanadium salt as a catalyst. Kornblum and Wade [94a] gave an unusual method of oxidation of secondary nitroalkanes to ketones with nitrous esters and sodium nitrite at room temperature:

$$R_2CHNO_2 + NaNO_2 + n\text{-}C_3H_7ONO \longrightarrow R_2CO + n\text{-}C_3H_7OH + NaNO_3 + N_2O. \qquad \mathbf{(11)}$$

The yield was up to 88% depending on nitroalkane.

6. *Nucleophilic displacement of the nitro group from nitroalkanes.* Such reactions were described by Kornblum [94b], Benn and Meesters [95]. The reactions consist in the substitution of the nitro group with aryls. The reaction of Kornblum will be described in the paragraph dedicated to arylnitroalkanes.

NITROMETHANE (Vol. I, p. 579)

Shaw [65] presented new data referring to the physico-chemical properties of nitromethane (as compared with those of methyl nitrite).

Shaw's data are as follows:

Density at 15°C	1.140
Boiling point	101°C
Melting point	−29°C
Heat of formation	−27 kcal/mol
Heat of vaporization	9,1 kcal/mol
Specific heat C_p^0	13.7 cal/mol deg
Activation energy of thermal decomposition	59.0 kcal/mol
Detonation velocity	
experimental	6300 m/s
calculated	6890 m/s

Some figures given by Meyer [66] are slightly different:

Density	1.1385
Boiling point	101.2°C.

He also gives vapour pressures:

1.3 millibar	at −29°C
10 millibar	0°C
32 millibar	20°C
140 millibar	50°C
283 millibar	80°C

A considerable amount of work has been dedicated to the problem of decomposition of nitromethane in gas-phase. They were reported in Vol. I (p. 579) and in the review article by Makovky and Lenji [67].

A few papers referring to flash photolysis should be mentioned: those by Norrish and co-workers [68], Pimentel and co-workers [69], Nicholson [70], McGarvey and McGrath [71].

Crawforth and Waddington [72] examined pyrolysis of nitromethane between 305° and 440° C. They found the reaction to be pressure dependent. Above 150 mm it is approximately of the first order

$$k = 10^{14.1} \text{ exp. } (-55 \text{ kcal/RT}) \text{ sec}^{-1}.$$

The main products are: methane, CO, N_2, NO, HCN and water. The authors suggested the mechanism through the initially formed methyl radical:

$$\begin{aligned} &\cdot CH_3 + CH_3NO_2 \longrightarrow CH_4 + \cdot CH_2NO_2 \\ &\cdot CH_3 + NO_2 \longrightarrow CH_3NO_2 \\ &\cdot CH_3 + NO_2 \longrightarrow CH_3O\cdot + NO \\ &\cdot CH_3 + NO \longrightarrow CH_3NO \end{aligned} \tag{12}$$

A few papers were dedicated to the decomposition of nitromethane in shock-tubes: Bradley [73], Hiraoka and Hardwick [74], Borisov and co-workers [75]. Glänzer and Troe [76] examined the decomposition of nitromethane highly diluted with argon in shock waves between 900 and 1500 I, and concentration of argon 1.5 × 10^{-6} and 3.5 × 10^{-4} mol/cm^3. A unimolecular reaction occurred:

$$CH_3NO_2 \longrightarrow \cdot CH_3 + \cdot NO_2 \tag{13}$$

The rate constant k is expressed by the equation:

$$K = 10^{17.1} \text{ exp } (-42 \text{ kcal/RT}) \text{ sec}^{-1}.$$

A subsequent reaction occurred between free radicals:

$$\cdot CH_3 + \cdot NO_2 \longrightarrow CH_2O + NO + \cdot OH \tag{14}$$

Shock initiation of liquid nitromethane (as compared with that of methyl nitrite) was given by Shaw [65].

Practical use of nitromethane as an explosive. The use of nitromethane is limited owing to its high volatility. According to Meyer [66] nitromethane was used in the U.S.A. for underground model explosion ('Pre-Gondola') in preparation for the nuclear charge technique, and for stimulation blasting in oil and gas wells.

Nitromethane can also be used as monergolic liquid fuel for rockets.

NITROETHANE, 1-NITROPROPANE AND 2-NITROPROPANE

Hermoni (Makovky) and Gruenwald [259] have described the thermal decomposition of nitroethane under pressure of ca. 38 atm. over the temperature range 245–258° and showed to be of the first order with a rate constant of the energy of activation of 42.2 kcal. This fits to figures obtained earlier.

The main products of the decomposition were: water, ethylene, carbon monoxide, methane, formaldehyde, nitric oxide, nitrogen dioxide, hydrogen cyanide, nitrogen and ethane.

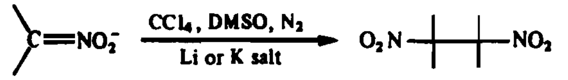
Glänzer and Troe studied a shock wave thermal decomposition in argon of nitroethane [77], 1- and 2-nitropropanes [78].

The following are data obtained (Table 42).

TABLE 42. Characteristics of shock wave thermal decomposition of nitroalkanes

	Nitroethane	1-Nitropropane	2-Nitropropane
Temperatures (K)	900–1350	915–1200	915–1200
Rate constant k sec^{-1}	$10^{15.9}$ exp (−57 kcal/RT)	2.3 x 10^{15} (−55 kcal/RT)	2.4 x 10^{15} (−54 kcal/RT)
Primary reaction step of C−N bond fission	$C_2H_5^{\bullet} + {}^{\bullet}NO_2$	$n\text{-}C_3H_7^{\bullet} + {}^{\bullet}NO_2$	$i\text{-}C_3H_7^{\bullet} + {}^{\bullet}NO_2$

2-Nitropropane can be subjected to dimerization under the action of alkali metals in carbon tetrachloride, DMSO in the atmosphere of nitrogen (15) [79]:



(15)

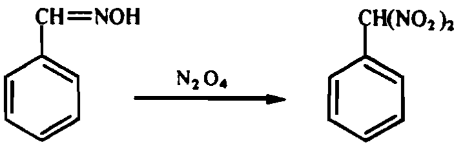
2-Nitropropane is widely used in the U.S.A. as a solvent, however its carcinogenic action has been reported [80].

ARYLNITROALKANES

Arylnitroalkanes form an interesting group of compounds: they combine the properties of the aromatic ring with those of nitroalkanes. The simplest is of course phenylnitromethane (Vol. I, pp. 96, 123, 275, 598). The chemistry of arylnitromethane was reviewed by Novikov and Khmelnitskii [81].

As has already been pointed out (Vol. I, p. 275) phenylnitromethane can be formed during the nitration of toluene, while using nitrogen dioxide as a nitrating agent.

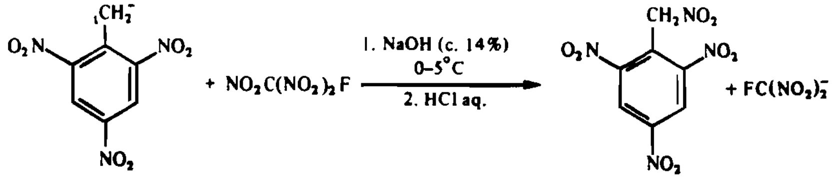
Higher nitrated derivatives of phenylnitromethane, among them those of derivatives of dinitro- and trinitromethane (Vol. I, p. 399) are important. The reaction of Ponzio [82] consists of acting with N_2O_4 on benzaldoxime: phenyldinitromethane results (16):



(16)

According to Fieser and Doering [83] the reaction should be carried out by gradually mixing solutions of benzaldoxime and N_2O_4 in dry ether at the temperature of boiling ether. The yield of the reaction produced in such a way was 38% lower than in the Ponzio original method (50%), but violent reaction is avoided.

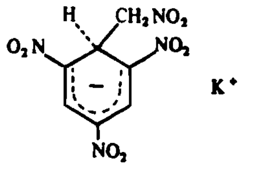
Derivatives of phenylnitromethane nitrated in the aromatic ring have again received (Vol. I, p. 598) attention, particularly in relation to the properties of TNT. Sitzmann, L. A. Kaplan and Angres [84] acted on 2,4,6-trinitrotoluene in alkaline medium with fluorotrinitromethane which is an alkaline nitrating agent and was prepared by Kamlet and Adolph [85]. The reaction (17) brought about the formation of 2,4,6-trinitrophenyl-nitromethane through the intermediate 2,4,6-trinitrotoluene anion (Chapter VI, reaction 5, and [86]):



(17)

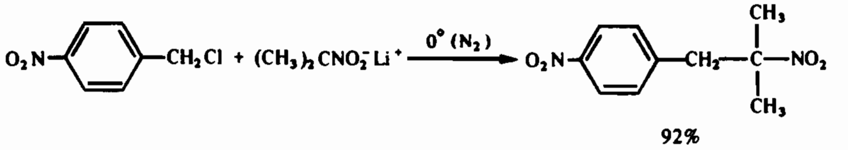
m.p. 116.5–118°C
89%

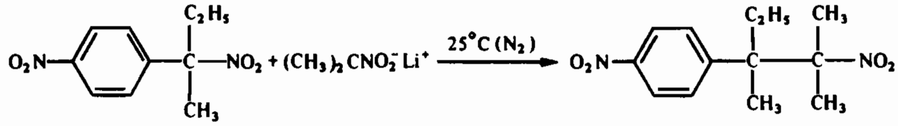
The same compound was obtained earlier by Russian workers [87] through the action of chloranil (as an oxidizing agent) on the σ-complex (I) of 2,4,6-trinitrotoluene with potassium salt of nitromethane.



I

A considerable amount of work was done by Kornblum and co-workers on the chemistry of arylnitroalkanes, particularly the *p*-nitrocumyl system with a side chain of branched nitroalkane in the *para* position to the nitro group [17, 88]. Two interesting reactions are given here as examples:


(18)


(19)

In both types of reaction lithium salts of nitroalkane were used and the reactions appeared to proceed via a chain mechanism in which radical anions and free radicals are intermediates.

A remarkable feature of reaction (19) is the substitution of the nitro group attached at tertiary carbon of the *p*-nitrocumenyl system. The reaction of the displacement of a nitro group from a saturated carbon atom through an anion has been described for the first time [88c].

In the same system of cumene a replacement of the nitro group by hydrogen was described by Kornblum and co-workers [88d]. The agent replacing the nitro group was sodium salt of methanethiol in an aprotic solvent:

$$R_3CNO_2 \xrightarrow[\text{room temp}]{CH_3S^-} R_3CH \qquad (20)$$

Łytko-Krasuska, Piotrowska and T. Urbański [89] reported the reaction of replacement of a secondary aliphatic nitro group by hydrogen while treating the nitro compound with potassium hydroxide in ethylene glycol at 120–140°C. The reaction proceeded by a radical anion mechanism. Ono and co-workers [121] described new methods of replacing the nitro group in aliphatic compounds by hydrogen. One of the methods consists in acting with *N*-benzyl-1,4-dihydronicotinamide [121a], and another [121b] by acting on tertiary and secondary nitro compounds with tin hydrides (or deuterides) of the type Bu_3SnH (or $Bu_3Sn\,D$). The treatment of nitro compounds with tin hydrides occurred by refluxing in benzene in the presence of azobisisobutyronitrile. $Bu_3Sn\,H$ was converted to the nitrite $Bu_3Sn\,ONO$.

Denitration of tetranitromethane and 1,1,1-trinitroethane by electrochemical reduction was reported by Petrosyan and co-workers [248, 249].

NITROCYCLOALKANES

Cycloalkanes, for example, cyclohexane can be nitrated with dilute nitric acid at a higher temperature (Vol. I, p. 84) or with nitrogen dioxide (Vol. I, p. 96).

Reich [98] reported that the best yield of nitrocyclohexane can be obtained with nitric acid of 30–50% HNO_3 at 120–140°C under 10–15 atm. The yield of nitrocyclohexane was up to 80%.

Nitrocyclohexane can be reduced to cyclohexane oxime to further transform into caprolactam. Several patents cover this method, but no practical application seems to have been found for it.

Nitro derivatives of cyclohexane can be obtained by the method of Severin (Chapter IV, formula 16) while reducing some nitroaromatic hydrocarbons with Grignard reagent or with sodium borohydride. Sodium borohydride reduced 1,3,5-trinitrobenzene to 1,3,5-trinitrocyclohexane (Vol. I, p. 252).

ESTERS OF NITROALCOHOLS AND UNSATURATED ACIDS

Nitroalcohols composed of nitroalkanes and formaldehyde have been esterified with acrylic and methacrylic acids in order to obtain products which could be subjected to polymerization. This is a part of the big programme on searching for solid propellants. The work on the above line was initiated by British Thomson-Houston Co. [235] described in a number of patents reviewed by Marans and Zelinski [236] who also gave an account of their own experiments. Nitroalcohols from nitromethane, nitroethane, 1-nitropropane and formaldehyde reacted with methyl esters of acrylic and methacrylic acids in the presence of concentrated sulphuric acid and cuprous chloride or toluene sulphonic acid and hydroquinone. Acrylic and methacrylic acid esters of nitroalkyls were formed through transestrification. They were polymerized at 100°C with benzoyl peroxide in an atmosphere of nitrogen. Only 2-methyl-2-2-nitropropyl ester gave a hard resin, whereas the other nitroalcohols gave viscous resins. The presence of the nitro group in the molecule seems to inhibit the polymerization in agreement with the findings described in Chapter IV.

INDUSTRIAL METHODS OF NITRATING ALKANES

Commercial Solvents Corporation, Inc., Terre Haute, Indiana, U.S.A. has a factory producing nitroalkanes by the method of Hess and co-workers (Vol. I, p. 86). In 1956 the annual production was in the order of 4400 tons. Also in Germany during World War II Badische Anilin – und Sodafabrik A.G., Ludwigshafen had a pilot plant for the daily production of 300 kg of nitroalkanes. It was working for three years (1939–1942) and in 1942 a larger plant capable of producing 1 ton daily was under construction, but was destroyed by bombing (according to Doležel [4]).

The industrial method for the nitration of propane is based mainly on the description by Doležel [4] in the German edition of the book by the author of the present monograph. Some details can also be found in the review article by Shechter and R. B. Kaplan [6b].

German Method of Nitration of Lower Alkanes

The method used in Germany at BASF (Ludwigshafen) was established by Schickh. It consisted of a stainless steel (V2A) nitrator in the form of a coil (1) (Fig. 29) submerged in a heating bath of molten sodium and potassium nitrate keeping the temperature at 400–450°C. A higher temperature was used for the nitration of methane and lower for higher hydrocarbons. Vapours of nitric acid (concentration 48% HNO_3) together with the hydrocarbon entered the coil from container (2). Molar ratio hydrocarbon:HNO_3 8–10 was maintained. The reaction products entered the cooling coil (3) and condenser (4). Liquid products were collected in the separator (5). Lower acid layer entered (6) and the upper layer was distilled off and collected in a condenser (7). The cyclon (8) retained the liquefied product and the gaseous hydrocarbons entered scrubbers (9) and (10) where they were washed with water, and then with sodium hydroxide solution in (11) to free them of traces of acids. The residual higher boiling products were retained in (12) and gaseous hydrocarbons returned to the nitrator. The gaseous oxidation and decomposition products were released through a valve (13).

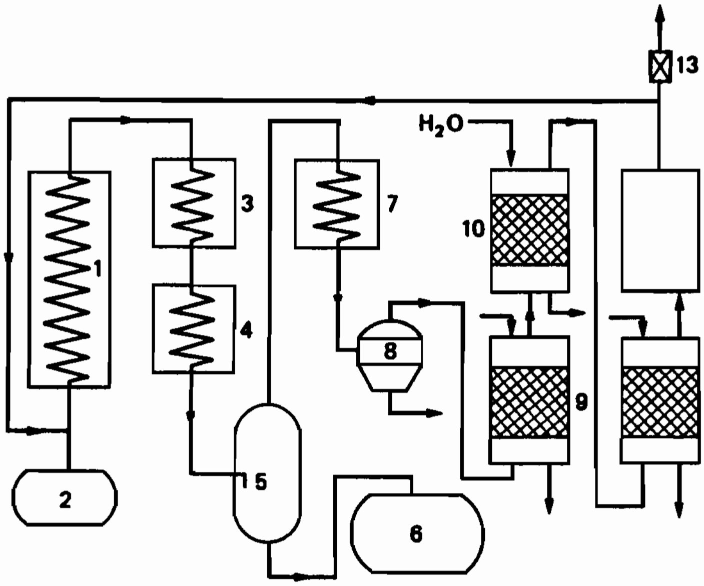


FIG. 29. Nitration scheme of Schickh used in Germany at BASF to nitrate alkanes according to Doležel [4].

The conversion of methane, ethane and higher hydrocarbons were 13%, 30% and 40–50% respectively. Methane was also nitrated under pressure of 10 atm., which increased the conversion to 20%.

Method of Commercial Solvents Corporation, Inc.

The nitration of hydrocarbons is carried out in a Stengel–Eagli [99] multisegment reactor (Fig. 30). It is usually composed of five segments.

The warmed alkane enters through (1) to the upper part of the nitrator. Nitric acid is injected through (2) and (3) to various segments of the nitrator. Electric heaters (4) maintain the correct temperature inside the apparatus. The constant temperature in the nitrator is maintained owing to the balance between the endothermic vaporization of nitric acid and exothermic heat of the reaction. Any deviations from the correct temperature are immediately avoided by valves (5) introducing air (or water). The products are evacuated through (6).

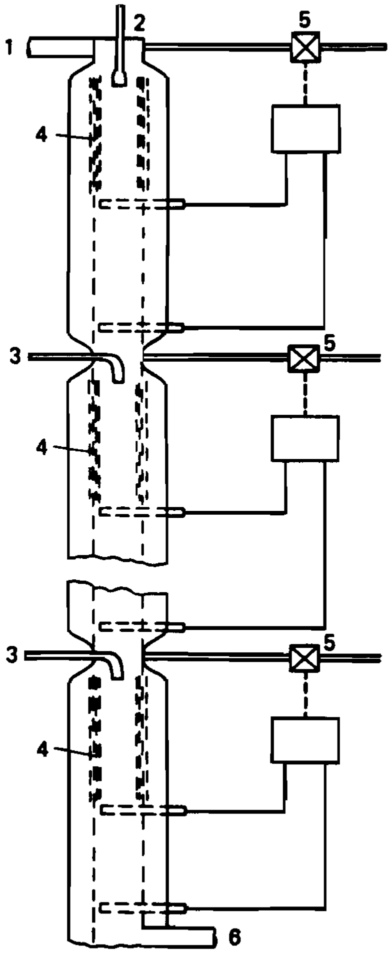


FIG. 30. Stengel–Eagli nitrator of alkanes used by Commercial Solvents Corp., Inc. according to Doležel [4].

The diagram of the method of nitration of propane is given in Fig. 31. Propane is supplied by pump (1) through a control valve (2), heater (3) and valve (4) to the upper part of the nitrator (5). Nitric acid (75–78% HNO_3) enters each segment of the reactor where the temperature of 400–435°C is kept constant. The temperature is maintained through a balance between the heat of nitration and the heat of evaporation of nitric acid, as previously mentioned. Heat regulators (6) and valves (7) can maintain the correct temperature in every segment. The temperature in every segment is measured by thermoelements.

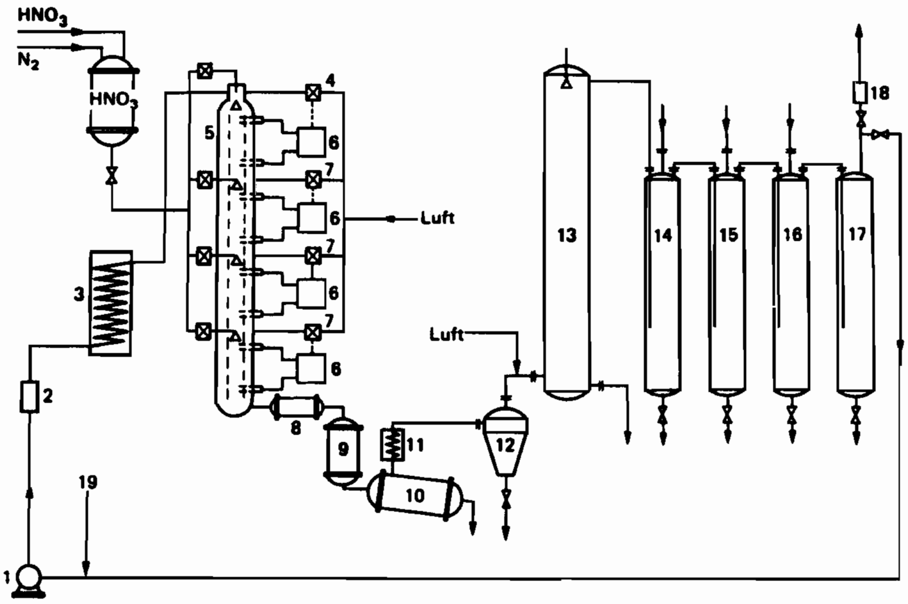


FIG. 31. Diagram of nitration of propane by Commercial Solvents Corp., Inc. according to Doležel [4].

The ratio propane:HNO_3 in the upper segment is of the order of 24.2:1 and the average ratio in the nitrator is 4.81:1. The pressure inside the nitrator is 8.75 kG/cm^2. If the temperature rises above 435°C, some water vapour is injected into the nitrator (higher concentrations of nitric acid tend to increase the temperature above the permitted limit).

The reaction gases are cooled intensely in (8) and condensed in (9). In (10) gaseous products enter (11) where they are cooled and in the cyclone (12) additional liquid fraction is obtained. The gaseous products containing nitrogen oxide enter the scrubber (13) together with air and NO is oxidized to NO_2. The scrubber is irrigated with water and thus nitric acid is recovered. Further washing of gases with water is achieved with scrubbers (14–17). In the last one (17) the flow rate of gases is lowered to free them from traces of water droplets. The gases leaving the last scrubber are rich with unreacted alkanes and return (through 19) to the nitrator. The gaseous by-products (e.g. N_2, CO, CO_2) leave the system through valve (18).

The conversion of propane to nitro compounds is in the order of 30–38%. The nitrated product is composed of 25% nitromethane, 10% nitroethane, 40% 2-nitropropane and 25% 1-nitropropane.

Distillation

The fractionation of nitro compounds is not a complicated problem, provided sufficiently efficient distillation columns are used. More difficult is the removal of acids (nitric acid, nitrogen oxides, organic acids), aldehydes and ketones, with water. The insoluble nitro compounds are subjected to azeotropic distillation. Water is separated as an upper layer and nitro compounds (with a small proportion of water on the bottom) are sent to distillation in order to separate the nitroalkanes. The flow-sheet is given in Fig. 32. The mixture of nitro compounds from an intermediate container (1) enters through a rotameter (2), pre-heater (3) into the upper part of column (4). The azeotropic mixtures go through condenser (5) to separator (6). The separated water returns to column (4) and the nitroalkanes through rotameter (7) enter column (8) where washing by a countercurrent method with sodium bisulphite to free them from traces of nitric and nitrous acid. Nitro alkanes having a lower density pass through the column upwards to enter column (9) where the products are washed with water. Water is pumped back to column (4) to recover the dissolved nitro alkanes. The separated oil passes to the intermediate vessel (10). From here it goes through rotameter (11) and pre-heater (12) into the distillation column (13). An azeotrop which is composed of nitro alkanes and water distils. From the bottom part of column (13) and sent to an intermediate vessel (14), rotameter (15) and eventually to column (16) where nitromethane distils out. The bottom part of column (16) contains nitromethane, and nitropropanes. The mixture of nitro alkanes enters through intermediate (17) and rotameter (18) to column (19). Nitroethane distils out from the latter. In the bottom of column (19) both nitropropanes remain. They are sent through a pump to the intermediate vessel (20) and from there to rotameter (21) into column (22) where 2-nitropropane distils out. The lower part of column (22) passes through (23) and rotameter (24) to column (25) where 1-nitropropane distils out.

Hazards of the Nitration of Alkanes

Matasă [100] discussed the problem of the hazards of the nitration of alkanes. In his remarkably important paper he considered:

1. Explosibility of gaseous mixtures,

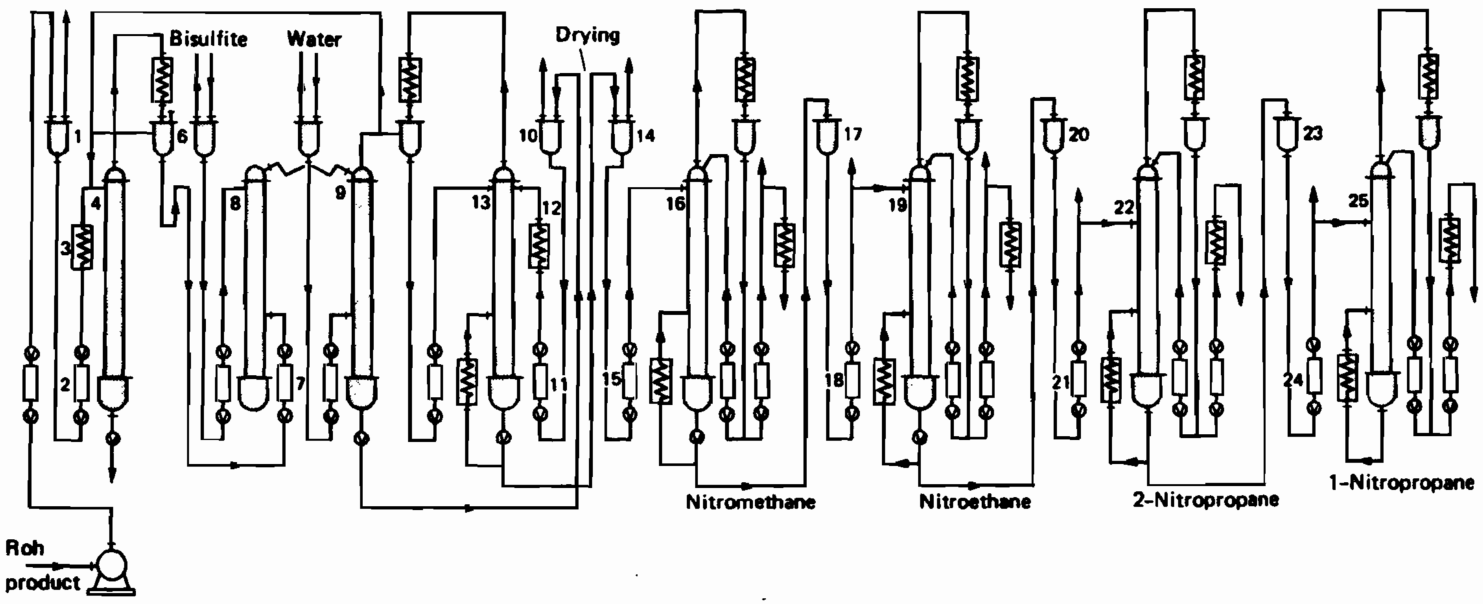


FIG. 32. Fractional distillation of nitroalkanes by Commercial Solvents Corp., Inc. according to Doležel [4].

2. Exothermic reactions of nitration and oxidation,
3. Reactivity of the liquefied product,
4. Explosive properties of nitro compounds.

Oxidation can be suppressed by adding molten salts to the reacting compounds, according to Albright [101]. Sodium nitrate is the most suitable salt probably breaking the reaction chain. Matasă summarized his work in a diagram – Fig. 33 based on the nitration of cyclohexane with nitric acid in a vapour phase. It gives the zone of nitration against the time of contact, molar ratio and reaction temperature.

The dangerous zone is divided into two parts: upper (1) in which pyrolysis mainly occurs and is manifested by rapid variations of pressure and explosions, and lower (2) where the reaction proceeds quietly, but the products are liable to react further. He also indicated a practical criterion of the reaction: the colour of the products. Yellow colour characterized the normal course of the reaction,

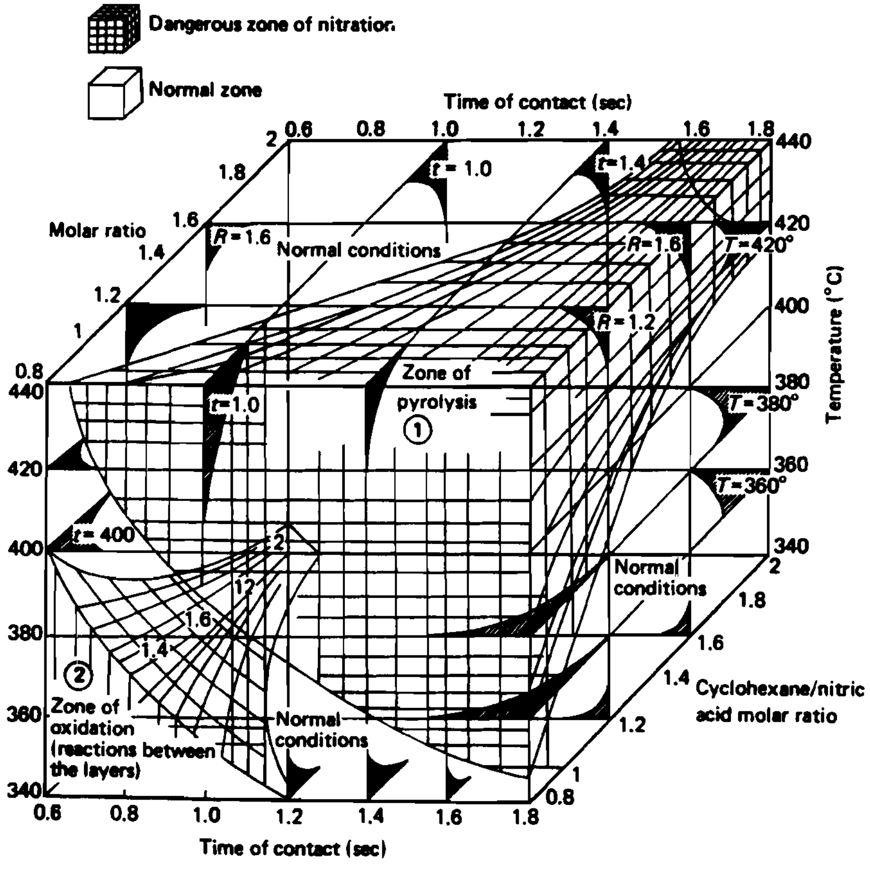


FIG. 33. Variation of the zone of nitration of cyclohexane according to Matasă [98].

whereas green and brown indicate a reaction between liquid products and too high temperature of the reaction or a too long contact time.

The molar ratio hydrocarbon–nitric acid was of the order of 10:1 and if oxygen was added it was up to 4 moles in quantity.

To reduce the cost of nitration (and probably to increase safety) hydrocarbon and nitrogen were used instead of pure hydrocarbon [6b]. The addition of oxygen to the system may offer the advantage of increasing the amount of heat evolved during nitration and thus helping to keep the reaction in adiabatical conditions. The oxygen helps in obtaining valuable oxidation products such as alcohols, aldehydes, ketones and carboxylic acid [6b].

According to the same source, at 395°C conversion of propane increased from 20% to 76% based on nitric acid used while the ratios of oxygen, propane and nitric acid changes from 0:11:1 to 3.8:11.4:1.

1,2-DINITROETHANE (Vol. I, p. 594)

Very little attention has been paid to this compound owing to its low stability. However, one paper can be mentioned which deals with the problem of conformation through the measurement of dipole moment [230]. The conclusion was that free rotation of NO_2 is most probable around the C–C axis. 1,2-Dinitroethane can be used as a source of hydroxylamine [231] and caprolactam from cyclohexanone [232].

2,2-DINITROPROPANE

This compound created a certain interest due to the presence of geminal nitro groups. The symmetry of the compound was examined by Buczkowski and Urbański [248] by infra-red and Raman spectra. The authors came to the conclusion that the compound belongs to C_{2F} symmetry (according to Herzberg classification).

Dinitroalkanes

The work of Asinger, Geiseler *et al.* [262] on 1.4-, 1.5-, 1.6- and 1.7-dinitrooctanes should be mentioned.

NITROALKENES (Vol. I, pp. 81, 95, 99, 107)

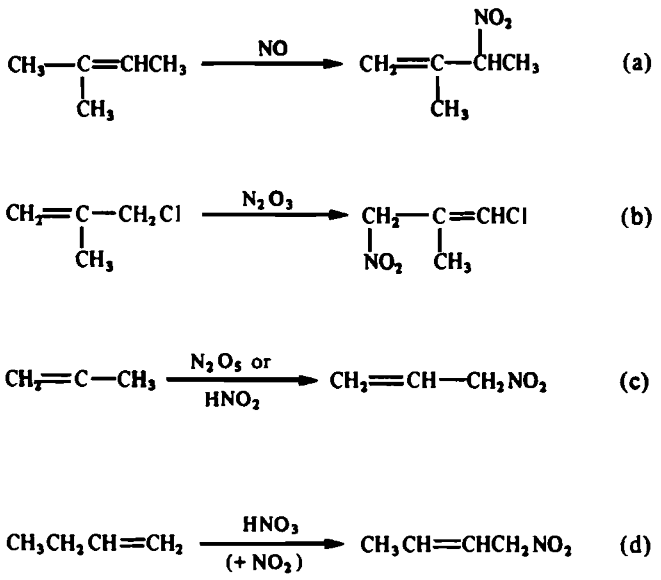
Nitroalkenes form an interesting group of compounds: they contain a strongly activating nitro group and a double bond which, under the influence of the nitro group, shows a particular activity.

The increasing interest in nitroalkenes is manifested by two monographs: those of Perekalin [8] and Novikov [9]. Some review papers dealing with the properties of nitroalkenes have also appeared [102].

Methods of Preparation of Nitroalkenes

The methods of preparation of nitroalkenes can be divided into several groups [6, 8, 9].

1. Action of nitrogen oxides and nitric acid on unsaturated hydrocarbons viz. NO (in the presence of catalytic amounts of NO_2), N_2O_3, N_2O_4, N_2O_5, HNO_3. Nitroalkenes are accompanied here by vicinal dinitro compounds, nitronitrites, nitronitrates, nitro–nitroso compounds, nitrosonitrites, nitrosonitrates, dinitrites and nitronitrates [6, 8, 9] (also Vol. I, pp. 96, 594). Some mononitro alkenes can also be formed. Here are a few examples taken from the above monographs and [12]:



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{NO} CH_2=\underset{CH_3}{\underset{|}{C}}-\overset{NO_2}{\overset{|}{C}}HCH_3 \quad (a)$$

$$CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2Cl \xrightarrow{N_2O_3} \underset{NO_2}{\underset{|}{CH_2}}-\underset{CH_3}{\underset{|}{C}}=CHCl \quad (b)$$

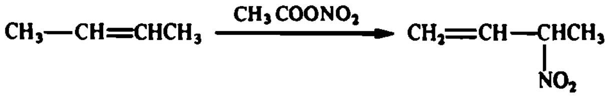
(21)

$$CH_2=C-CH_3 \xrightarrow[HNO_3]{N_2O_5 \text{ or}} CH_2=CH-CH_2NO_2 \quad (c)$$

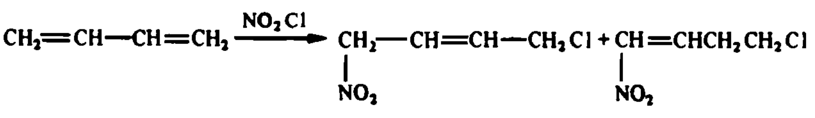
$$CH_3CH_2CH=CH_2 \xrightarrow[(+NO_2)]{HNO_3} CH_3CH=CHCH_2NO_2 \quad (d)$$

Reaction (21a) needs some explanation as regards its mechanism. Nitrogen oxide is disproportionated into nitrogen and nitrogen dioxide and the latter acts as the nitrating agent.

Acetylnitrate and nitronium chloride can also produce nitroalkenes while acting on alkenes:



$$CH_3-CH=CHCH_3 \xrightarrow{CH_3COONO_2} CH_2=CH-\underset{NO_2}{\underset{|}{C}}HCH_3 \quad (22)$$



$$CH_2=CH-CH=CH_2 \xrightarrow{NO_2Cl} \underset{NO_2}{\underset{|}{CH_2}}-CH=CH-CH_2Cl + \underset{NO_2}{\underset{|}{C}}H=CHCH_2CH_2Cl \quad (23)$$

The reaction of V. Meyer can also be used: for example, allyl bromide reacts with silver nitrite to yield 3-nitropropenel: $CH_2 = CH-CH_2NO_2$.

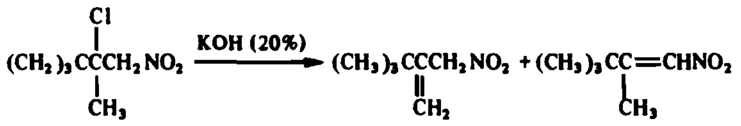
2. Dehydration of nitroalcohols and their esters. Nitroalcohols obtained by the Henry method can be readily dehydrated with phthalic anhydride (Vol. I, p. 596).

In some instances it has been found that esters can give purer substances [103]. According to Gold [104a] nitroalkenes can be obtained in good yield (up to 85%) by vapour phase catalytic cleavage of esters of nitroalcohols, for example:

$$CH_3COOCH_2CH_2NO_2 \xrightarrow[(300-400°C)]{\Delta} CH_2{=}CHNO_2 + CH_3COOH \qquad (24)$$

As a catalyst calcium–magnesium phosphate appeared to be the best.

Dehydrohalogenation of halogenonitro alkanes, for example (25):

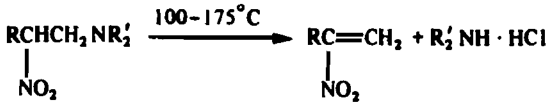


$$(CH_3)_3C\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2NO_2 \xrightarrow{KOH\ (20\%)} (CH_3)_3C\underset{\underset{CH_2}{\|}}{C}CH_2NO_2 + (CH_3)_3C\underset{\underset{CH_3}{|}}{C}{=}CHNO_2 \qquad (25)$$

Vinyl product (1) was mainly formed.

Denitration of polynitroalkanes with potassium hydroxide can also produce nitroalkenes (Vol. I, p. 98, IX–X).

Deamination of Mannich bases hydrochlorides can also furnish nitroalkenes [9] through pyrolysis (26):



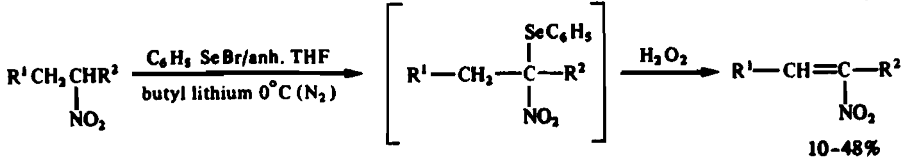
$$R\underset{\underset{NO_2}{|}}{C}HCH_2NR'_2 \xrightarrow{100-175°C} R\underset{\underset{NO_2}{|}}{C}{=}CH_2 + R'_2NH \cdot HCl \qquad (26)$$

For more information about the variety of reactions leading to nitroalkenes see [8, 9].

Recent Reactions of Formation of Nitroalkenes

Dehydrogenation of nitroalkenes was recently reported by Japanese workers: Sakakibara *et al.* [105]. The reaction consists in acting with phenylselenenyl bromide on nitroalkanes in the presence of butyl-lithium. Nitrophenylselenoalkanes are formed in the first instance, and decompose under the action of hydrogen peroxide (27):

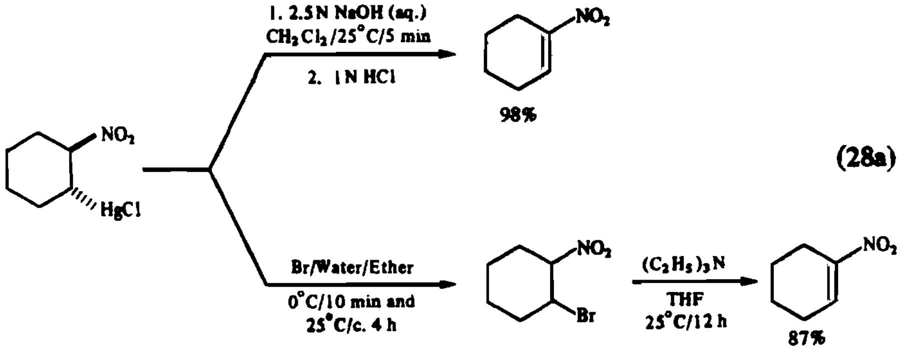
(27)



$$R^1CH_2\underset{\underset{NO_2}{|}}{C}HR^2 \xrightarrow[\text{butyl lithium } 0°C\ (N_2)]{C_6H_5SeBr/\text{anh. THF}} \left[R^1{-}CH_2{-}\overset{\overset{SeC_6H_5}{|}}{\underset{\underset{NO_2}{|}}{C}}{-}R^2 \right] \xrightarrow{H_2O_2} \underset{10-48\%}{R^1{-}CH{=}\underset{\underset{NO_2}{|}}{C}{-}R^2}$$

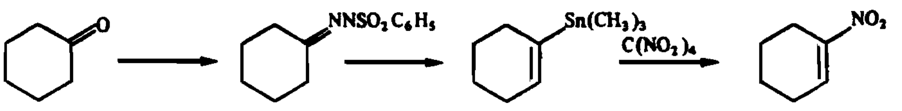
Nitroalkenes resulted with yields of 50–83%.

Corey and Estreicher [106] developed new methods for the preparation of conjugated 1-nitrocycloalkenes (28). They used nitromercurial chlorides (28a) obtained by Bachman and Whitehouse [107] or vinyl stannanes. The latter were transformed into conjugated nitroalkenes by the action of tetranitromethane (28b):

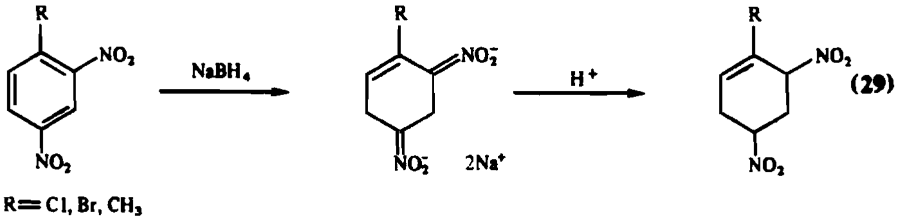


(28a)

(28b)



Severin and co-workers [108] gave an original method for the preparation of dinitrocyclohexene derivatives by acting with sodium borohydride on aromatic dinitro compounds (29)



(29)

Chemical Properties of Nitroalkenes

Nitroalkenes are pale yellow coloured liquids with boiling points slightly lower than those of corresponding nitroalkanes. They are lacrimatory substances with a pungent odour. They produce irritation of the mucous membranes, respiratory tract and skin.

They are susceptible to many addition reactions and anionic polymerization.

Addition Reactions

Addition of water and hydrogen sulphide yield alcohols and mercaptans respectively. Addition of alcohols and mercaptans yields nitroethers and nitrothioethers respectively. Halonitroalkanes are formed by the addition of halogens or hydrohalogenides. Nitrogen oxides yield dinitroalkanes. Nitronium chloride and nitrosyl chloride furnish nitrochloroalkanes. The addition of cyanohydride yields nitrocyanoalkanes. Amino nitroalkanes were obtained by adding ammonia or amines. Grignard reagent with a subsequent hydrolysis yielded dialkylhydroxylamine or nitroalkanes. Michael addition to nitroalkenes was also recorded. Nitroalkenes are important philodienes in the Diels-Alder reaction [104b].

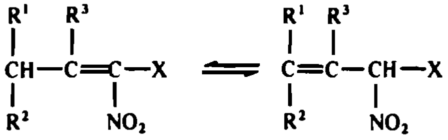
A more detailed description of these reactions is outside the scope of this book but can be found in [1], in monographs [8, 9] and they are mentioned in a review article by Jagur-Grodzinski [109].

Among the recent papers an addition of allilesilan to α-nitroalkenes [110] was described.

A particular kind of addition is the polymerization of nitroalkenes – this will be discussed in a separate paragraph.

Isomerization

The isomerization of nitroalkenes is one of the most interesting properties of these compounds. The isomerization can be depicted by a diagram [102a] (30):



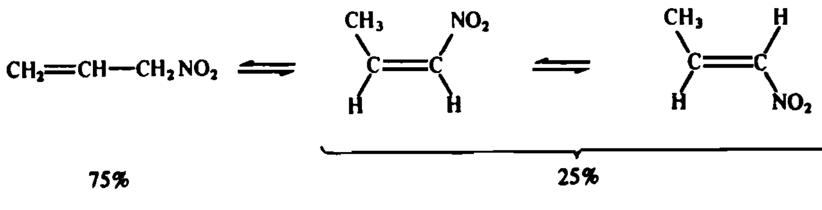
$$\underset{R^2}{\overset{R^1}{CH}}-\overset{R^3}{C}=\underset{NO_2}{C}-X \rightleftharpoons \underset{R^2}{\overset{R^1}{C}}=\overset{R^3}{C}-\underset{NO_2}{CH}-X$$

(30)

X can be H, halogen, COOH, CN etc.

Isomerization occurs under the action of catalytic amounts of bases (KOH, $(C_2H_5)_3N$).

Such isomerizations were described by Shechter and Shephard [111], Bordwell and Gerbich [112]. Witanowski, T. Urbański and co-workers [113] examined the isomerization of 3-nitropropene by catalytic amounts of sodium methoxide. By using the NMR technique they established the existence of the equilibrium (31):



(31)

A number of papers by Hesse have appeared on isomerization under the action of bases [114] and on the mechanism of isomerization by Leseticky and Prochazka [115], Piotrowska and Kochany [116], Werkhoff [117].

Reduction of the Double Bond

Reduction of the double bonds in nitroalkenes without the reduction of the nitro group can be carried out with sodium borohydride: when applied to nitroalkenes the nitroalkanes can be obtained (the method of Severin [108b]).

Polymerization

The ease of polymerization of nitroalkenes has attracted the attention of chemists for a long time. In particular the polymerization of nitroethylene has been extensively studied. An excellent critical description has been given by Jagur-Grodzinski [109]. Nitroethylene polymerizes readily in the presence of alkalis. Polymerization is exothermic (21.78 kcal/mol at 20°C) and in the presence of strong alkalis can be explosive.

Secondary and tertiary amines and phosphines have been found to be effective but not very strong catalysts. By polymerizing at –75°C in dimethylformamide high molecular weight linear polymer was obtained. Polymerization has an ionic character.

Poly(nitroethylene) prepared at low temperature is a white fibrous material soluble in dimethylformamide. When polymerization is carried out at room temperature it is a yellowish coloured powder of low molecular weight. Lauenberger [103] found that poly(nitroethylene) obtained by anionic polymerization is of relatively low molecular weight (M = *ca*. 500). He also obtained co-polymers with acrolein or acrylonitrile using tri-*n*-amyloamine as a catalyst at 0°C. The co-polymers were in the form of grains or flakes. He established that nitroethylene cannot be subjected to radical polymerization under the action of benzoylperoxide or 2-azodiisobutylnitrile.

Polymerization of 2-nitro-1-propene is less vigorous (the heat of polymerization is 13.0 kcal/mol at 20°C). The polymer is a viscous liquid or a brittle solid.

The chemical stability of the polymers of both nitroethylene and 2-nitro-1-propene is low. This is partly due to the traces of catalysts present in the polymers which can act as decomposition catalysts. Poly(nitroethylene) turns yellow and then dark brown coloured after a few hours at room temperature and at 60°C respectively. In the latter case it becomes insoluble in organic solvents. According to Farmer [118] poly (nitroethylene) gives a negative 'vacuum stability test' (Vol. II, p. 25) – an explosion occurs at 120°C. Nevertheless the polymer freed from the polymerization catalyst (by boiling in tetrahydrofurane acidified with acetic acid) shows good stability, comparable to that of nitrocellulose.

So far polynitroethylene (and propylene) do not seem to have a practical application [119].

Characteristics of the main nitroalkenes are given in Table 43.

TABLE 43. Physical constants of some nitroalkenes

Compound	Formula	Boiling point (°C)	Specific gravity	UV absorption nm
1-Nitroethylene	$CH_2=CH-NO_2$	98.5°	1.073	227
2-Nitro-1-propene	$CH_2=\underset{\substack{\vert \\ CH_3}}{C}-NO_2$	57° (100 m kg)	1.0643	225
1-Nitro-1-propene	$CH_3-CH=CH-NO_2$	54° (28 mmHg)	1.0661	229 235

NITROACETYLENES

A few representatives of this group of compounds were recently obtained by Russell *et al.* [122] by acting with lithium acetylides on 2-chloro-2-nitropropane or 2,2-dinitropropane in tetrahydrofurane:

$$RC\equiv CLi + \underset{X=Cl,\ NO_2}{X-C(CH_3)_2NO_2} \longrightarrow \underset{20-53\%}{RC\equiv C-C(CH_3)_2NO_2 + LiX} \qquad (32)$$

POLYNITRO ALIPHATIC COMPOUNDS (Vol. I, p. 587)

Over the last three decades considerable attention has been given to the search for energy rich propellants and explosives among polynitro aliphatic compounds. An excellent review has been given by Noble, Borgardt and Reed [5] on such compounds.

However, most of the polynitro aliphatic compounds show relatively low stability and high sensitivity and these facts have limited their practical usefulness [119]. The author of the present book will describe only:

(1) general methods of formation of polynitro compounds,
(2) physico-chemical, chemical and explosive properties of the most important compounds for which a practical application can be found or have already become commercial products.

NITRATION OF HYDROCARBONS

The problem of whether the nitration of hydrocarbons can yield dinitro compounds became controversial. According to T. Urbański and Słoń (Vol. I, p. 95) the nitration of hydrocarbons from propane to *n*-heptane at 220–230°C with a great excess of NO_2 can yield viscous oil containing dinitro products (10–22%

of the total quantity of products). Grundman and Haldenwanger (Vol. I, p. 84) obtained gem-dinitrocyclohexane when cyclohexane was nitrated at 122°C under pressure of 4 atm. Asigner and Oltay [123] nitrated 1-nitrooctane and obtained a mixture of dinitro products with various positions of the nitro groups. Statistical distribution equal to all positions from $C_{(2)}$ to $C_{(7)}$ (*ca.* 15%) was found.

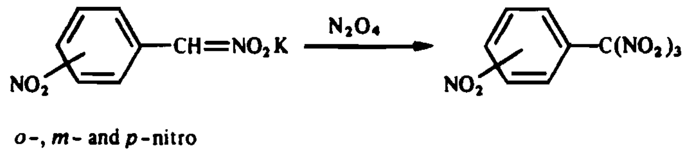
It seems that the high temperature of nitration applied by Hess and co-workers (Vol. I, p. 86) 410–430°C was too high for dinitro compounds and they decomposed.

The nitration of olefins can sometimes give polynitro compounds [124] (33)

$$CH_3CH{=}C(NO_2)CH_3 \xrightarrow{70\%\ HNO_3} CH_3CH(NO_2)C(NO_2)_2CH_3. \qquad (33)$$

Nitration through the addition of nitric acid or nitrogen oxides to alkenes forms a special chapter. This was described in Vol. I, pp. 96–99 and reviewed [5–9].

Only a few typical reactions will be given here leading to a higher number of nitro groups. Such is the reaction of Novikov and co-workers [124] (34)

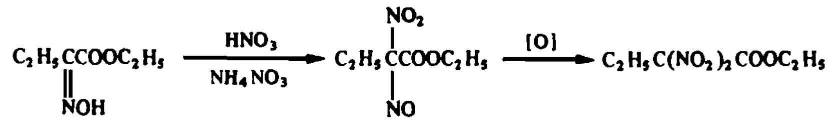


(34)

Parker, Emmons and co-workers [125] described the method of preparation of trinitroacetonitrile

$$NC{-}CH_2COOH{+}3HNO_3 + 3SO_3 \xrightarrow{CCl_4} NC{-}C(NO_2)_3 + CO_2 + 3H_2SO_4. \qquad (35)$$

The oxidation of oximes and other hydroxylamine derivatives followed by the action of nitric acid has also been described [126] (36)



$$C_2H_5\underset{\underset{NOH}{\|}}{C}COOC_2H_5 \xrightarrow[NH_4NO_3]{HNO_3} C_2H_5\overset{NO_2}{\underset{NO}{C}}COOC_2H_5 \xrightarrow{[O]} C_2H_5C(NO_2)_2COOC_2H_5 \qquad (36)$$

Substitution of Halogen

A modification of the Victor Meyer reaction for long chain hydrocarbons (over C_8) was given by Kornblum (Vol. I, p. 127) [127] and reviewed by the same author. Another modification of the V. Meyer reaction was given as early as 1870 by ter Meer [128]. It applies to 1-nitro-1-haloalkanes. By acting with sodium nitrite on the sodium salt of 1-nitro-1-haloalkanes *gem*-dinitroalkanes are formed. The reaction was reviewed and studied by Hawthorne [129]. The reaction has a number of limitations, more universal is the ingenious method by R. B. Kaplan and Shechter [130] for preparing *gem*-dinitro alkanes from nitroalkanes. It gives positive results where the method of ter Meer fails.

The reaction consists of an oxidation–reduction process of 1-nitroalkanes and can be depicted by scheme (37)

$$R_2C{=}NO_2^- + AgNO_3 + NaNO_2 \xrightarrow[0-30^\circ C]{H_2O} \underset{90\%}{R_2C(NO_2)_2} + 2\,Ag \qquad (37)$$

The reaction proceeds smoothly in alkaline aqueous media with silver nitrate and inorganic nitrites. Because of this method Feuer and colleagues [131] were able to obtain α, α, ω, ω-tetranitro alkanes. With four carbon atoms of chain of the nitroalkane, the yield of tetranitro compound could reach 84%.

Electrolytic Methods

The electrolytic coupling of primary and secondary nitroalkanes in basic medium has been reported by Bahner [132]. Another reaction yielding gem-dinitroalkanes was carried out with silver anode [133]. There is a similarity between this reaction and the Kaplan–Shechter method as silver is generated at the anode.

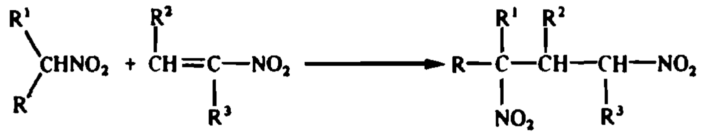
ADDITION REACTIONS

Two addition reactions were applied to produce polynitro aliphatic compounds:

(1) Michael addition,
(2) Diels–Alder addition.

Michael Addition

One of the first papers was by Lambert and Piggott [134] who studied the reaction of α-nitroalkenes (i.e. conjugated nitro compounds) with nitroalkanes:



(38)

Shechter and Cates [135] studied the addition of nitroform to α,β-unsaturated ethers to produce α-trinitromethyl ethers in good yield. Hamel [136] tried Michael addition and Mannich reaction and obtained a number of polynitro compounds.

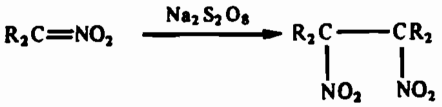
Diels–Alder Addition

Relatively less attention has been paid to the Diels–Alder reaction producing polynitro compounds. Gold and co-workers [137] successfully used 2,2-dinitromethanol which in the course of refluxing lost water to produce 1,1-dinitroethylene, a very strong dienophile:

$$CH(NO_2)_2CH_2OH \xrightarrow{\Delta} CH_2 = C(NO_2)_2 + H_2O. \tag{39}$$

OXIDATIVE DIMERIZATION

Shechter and R. B. Kaplan [138] obtained *vic*-dinitroalkanes by the oxidation of primary and secondary alkanes (in alkaline medium) with sodium persulphate (40):



$$R_2C{=}NO_2 \xrightarrow{Na_2S_2O_8} \underset{NO_2}{\underset{|}{R_2C}}{-}\underset{NO_2}{\underset{|}{CR_2}} \tag{40}$$

α, ω-DINITROALKANES

α, ω-Dinitroalkanes were prepared in a classical way by the V. Meyer method of reacting diiodides and bromides with silver nitrite [5]. The modification of the method by Kornblum (Vol. I, p. 127) [127] using sodium nitrite in dimethylformamide made the compounds more accessible. Feuer, Nielsen and Colwell [139] used α, ω-dinitroalkanes for the Henry reaction with formaldehyde to obtain diols which can be nitrated to obtain compounds with two *O*-nitro groups.

gem-Dinitroalkanes (1,1-Dinitroalkanes)

A considerable number of papers have been published on the properties of gem-dinitroalkanes and their fluorine derivatives by Nazin, Manelis and Dubovitskii [252] and kinetics of their thermal decomposition. The energy of dissociation of the bond C—N was found to be 47–48 kcal/mol.

TRINITROMETHANE (NITROFORM) DERIVATIVES (Vol. I, p. 587)

The last two decades of searching for high energy compounds were dedicated to products with the trinitromethyl group. The growing interest in these compounds is reflected in two symposia [1] and [2] and in an excellent review by L. A. Kaplan [140].

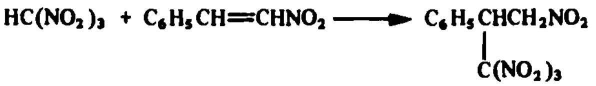
The method of manufacture of nitroform from acetylene found as early as 1900 by Baschieri (Vol. I, p. 587) was described by Orton and McKie [141]. It became possible to convert one of the carbons of acetylene to nitroform through a mercury catalysed oxidation–nitration process with nitric acid. Nitroform is an intermediate product of nitration and yields tetranitromethane under the action of excess nitric acid (Vol. I, p. 594). The method was developed during World War II by Schultheiss [142] and Schimmelschmidt [143] on a large laboratory scale with the aim of producing tetranitromethane. Later the industrial scale method for the manufacture of nitroform was created by Wetterholm [144] (and is described below).

Properties of Nitroform

Trinitroalkanes deriving from nitroform have a low intensity absorption band at *ca.* 280 nm and with hydrazine give a strong absorption at 350 nm. This fact can serve to spectrophotometric analysis [145, 146].

Three electron accepting groups in nitroform produce very strong acid properties. Its pK_a is 0.1 [146].

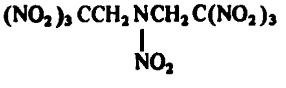
Nitroform is a nucleophile and can be added to nitroalkenes at low temperature (*ca.* 0°C) in methanol with a good yield. This was done by the pioneering work of Novikov and co-workers [246, 247] and L. A. Kaplan and Hine [147], for example (41):



$$HC(NO_2)_3 + C_6H_5CH{=}CHNO_2 \longrightarrow \underset{\displaystyle C(NO_2)_3}{C_6H_5\overset{}{C}HCH_2NO_2} \qquad (41)$$

Addition to carbonyl compounds is an important reaction, for example, nitroform with formaldehyde yields 2,2,2-trinitroethanol (Vol. I, p. 588) [148]. As previously mentioned (Vol. I, p. 588) the reaction is strongly exothermic. According to Wetterholm [153] it evolves 8.56 kcal/mol. The next step is the Mannich reaction which offers synthetically valuable trinitromethyl amines and their derivatives. The simplest Mannich base is made of nitroform, formaldehyde and ammonia:

$$(NO_2)_3CCH_2NHCH_2C(NO_2)_3 \qquad \textbf{II}$$

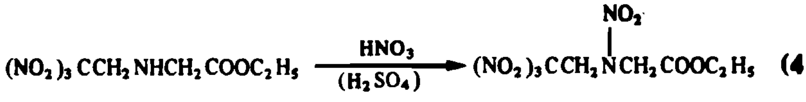


$$(NO_2)_3CCH_2\underset{\displaystyle NO_2}{N}CH_2C(NO_2)_3 \qquad \textbf{III}$$

Product II is unstable and can decompose on standing but after nitration, III shows a much better stability [149]. This observation is in agreement with that of Feuer and Swarts [150] and in the work of Feuer, Bachman and co-workers

[151] who described reactions of nitroform with formaldehyde and amino acid esters to form *N*-trinitroethylamino acid esters.

The products were unstable, but after nitration stable *N*-nitro compounds resulted (42):



$$(NO_2)_3CCH_2NHCH_2COOC_2H_5 \xrightarrow[(H_2SO_4)]{HNO_3} (NO_2)_3CCH_2\overset{NO_2}{\overset{|}{N}}CH_2COOC_2H_5 \qquad (42)$$

Wetterholm [153] reacted 2,2,2-trinitroethanol with urea to obtain *N,N'*-bis (trinitroethyl) urea ('DiTeU') (IV) a new strong explosive, near to Cyclonite with regard to its power.

$$(NO_2)_3CCH_2NHCONHCH_2C(NO_2)_3$$

m.p. 191°C

IV

It is described on – p. 259, reaction (56) [250].

Another interesting and new approach to using 2,2,2,-trinitroethanol as an explosive was given by Japanese authors: Shiino, Fujiwara and Kusakabe [214].

Frankel [152] described a number of Michael type additions of nitroform to unsaturated compounds. The most interesting was that of addition to nitroethylene.

Ville [234] also described some Mannich bases, their *N*-nitro derivatives and acrylic ester of trinitroethanol. He also obtained the product of addition of nitroform to acrylic esters.

The interesting properties of mercuric salt of nitroform were extensively studied by Novikov and co-workers [9a].

They described (among other reactions) the use of it for the mercuration of aromatic and heterocyclic compounds and the addition of mercuric salt to alkenes and their derivatives.

The thermal decomposition of nitroform and some of its fluorine derivatives were extensively studied by Mazin, Manelis and Dubovitskii [252, 253].

They obtained ortho-esters of 2,2,2-trinitroethanol: such as the orthoformate (TNEOF) (V) and orthocarbonate (TNEOC) VI by reacting 2,2,2-trinitroethanol with chloroform and carbontetrachloride respectively in the presence of anhydrous ferric chloride. The yields were 74% and 89% respectively.

$$HC[OCH_2C(NO_2)_3]_3 \qquad C[OCH_2C(NO_2)_3]_4$$

V **VI**

m.p. 128°C m.p. 161°C

The substances appear to be of good stability. They are soluble in polar solvents. The saturated solutions of V and VI in nitromethane are 1.53 and 1.48 respectively. Their oxygen balance is +0.10% and +0.13% respectively.

The substances show very low sensitivity to impact (they do not explode when 5 kg weight was dropped from 50 cm).

Data on the explosive properties of solutions of both substances in nitromethane and nitroethane are given in Table 44.

TABLE 44. Explosive properties of TNEOF and TNEOC with nitroalkanes

Composition		Density g/cm^3	Detonation velocity m/s
TNEOF Nitromethane	50 50	1.356	7075
TNEOF Nitromethane	77.1 22.9	1.533	7575
TNEOC Nitromethane	69.7 30.3	1.480	7350
TNEOF Nitromethane	77.0 23.0	1.496	7440

Manufacture of Nitroform

The manufacture of nitroform from acetylene was described by Wetterholm [144]. The flow-sheets of the process are given in Figs 34 and 35.

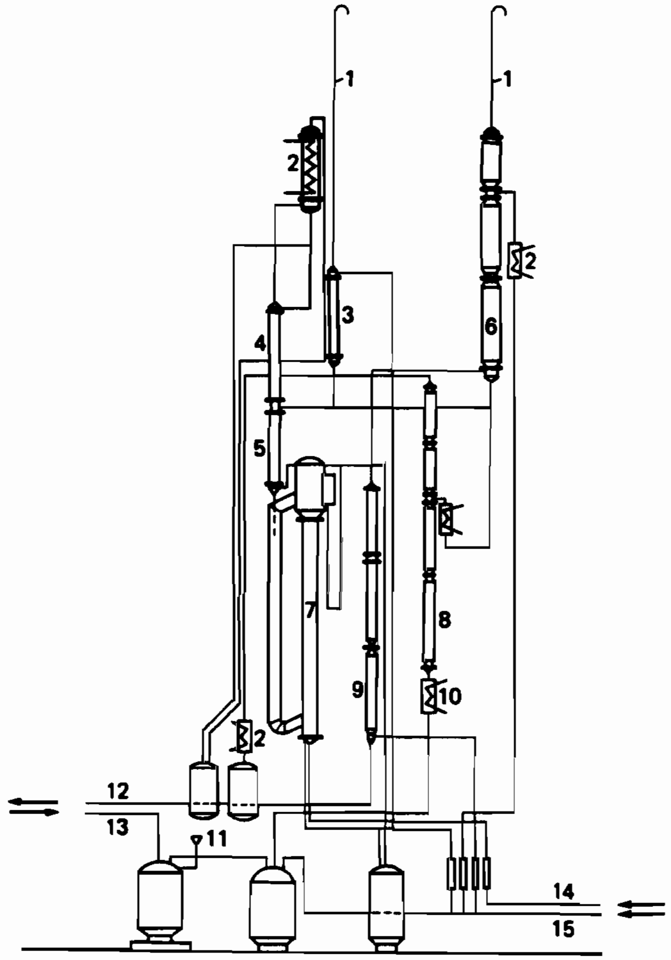
Figure 34 depicts a nitrator where the oxidation–nitration takes place combined with a recovery system for the large amount of nitrogen oxides evolved.

Figure 35 presents a distillation system consisting of fractionating towers and an evaporator.

The equipment includes a concentration of dilute nitric acid formed in the course of the reaction. This is a standard procedure and is not included in the figures.

The reaction of nitration is carried out at 45–48°C. From the overflow the products of the reaction go to a stripper where they are freed from nitrogen oxides with air in a countercurrent with cold nitric acid at −15°C. The scrubbing acid is used as part of the acid feed. The gases generated during nitration consist of CO_2, CO, nitrogen oxides and some nitroform. The gases pass through a hot scrubber which retains nitroform. Next is a packed tower where pure N_2O_4 is condensed in a cooler. The waste gases are composed of 76% CO_2, 12% CO, 6% N_2, 6% HNO_3.

The extraction of nitroform from a strong nitric acid consists of two steps:



1 Waste gases
2 Cooling liquid
3 Cold scrubber
4 N_2O_4 distillation
5 Warm scrubber and stripper (N_2O_4)
6 N_2O_4 scrubber
7 Nitrator
8 Bleaching tower
9 Nitrogen oxide stripper
10 Water
11 Catalyst
12 Nitration solution out
13 Nitric acid in
14 Acetylene
15 Air in

FIG. 34. Production of nitroform. Nitration system according to Wetterholm [138].

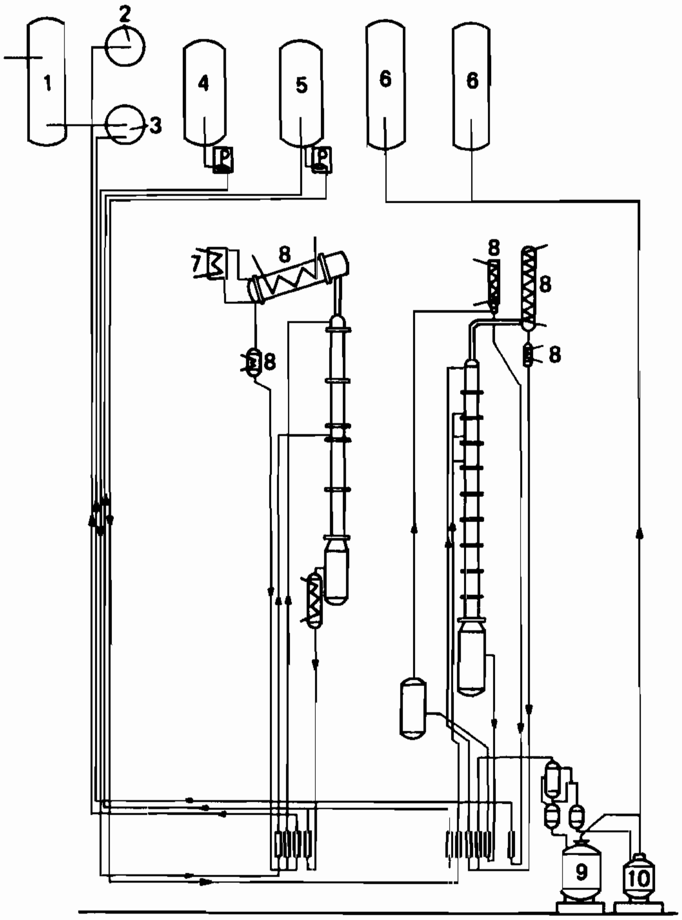


FIG. 35. Production of nitroform (Nif). Distillation system according to Wetterholm [138].

(1) Distillation of the acid until the composition reaches the minumum azeotrop. Nitroform does not distil during this period.
(2) Addition of water and distillation of nitroform with water.

The overall yield of transformation of acetylene to nitroform is *ca.* 74%.

TETRANITROMETHANE (TNM) (Vol. I, p. 588)

There is an increasing interest in tetranitromethane as a source of energy rich explosives and this is manifested by a number of papers related to the physical and chemical properties of the compounds. An excellent review on TNM was given by Altukhov and Perekalin [156].

Physical and Physico-chemical Properties of TNM

The setting point is +13.75 [157a], +14.2 [157b] (an incorrect figure was given in Vol. I, p. 588); boiling point 126°C [157]; specific gravity d_4^{15} = 1.6484, d_4^{20} = 1.6218, mol. refraction $MR_D = 31.39$ (calculated 29.30) [158].

The ultraviolet spectrum is manifested by the main band at 280 nm, the infrared spectrum has two strong bands 1618 and 1266 cm^{-1} corresponding to asymmetric and symmetric vibrations respectively, and a number of less prominent bands at 1645, 1439, 1370, 990 and 973 cm^{-1} [159]. Examination of the infrared spectra of TNM at different temperatures (–40° to –126°C) [160] indicated that TNM exists in two crystalline forms with their transition point at –99.8°C.

The mobility of one nitro group of TNM suggested originally that one nitro group possesses a different structure from the others, for example, the nitrite or peroxy structure. This proved to be wrong and it has now been firmly established by X-ray analysis that TNM possesses a perfectly symmetrical structure [161] – Fig. 34. This was substantiated by dipole moment measurement which has been found to be equal to 0 within the experimental error. Electron diffraction also confirmed the symmetrical structure of TNM [162].

Quantum chemical calculation was carried out by Shlyapochnikov and Gagarin [163]. It was shown that the electron increased at the oxygen atoms of the nitro groups of TNM and was reduced at the nitrogen and carbon atoms. This is marked in Fig. 36.

The energy of formation of TNM is according to different authors 4.7–8.9 kcal/mol and enthalpy of formation –18.5 kcal/mol. [156]. Heat of decomposition – equation (43)

$$C(NO_2)_4 \longrightarrow CO_2 + 3O_2 + 2N_2, \tag{43}$$

is according to various sources 89.6–102.9 kcal/mol [156]. The energy of the C – N bond was calculated: 38.2–39.3 kcal/mol [164, 165].

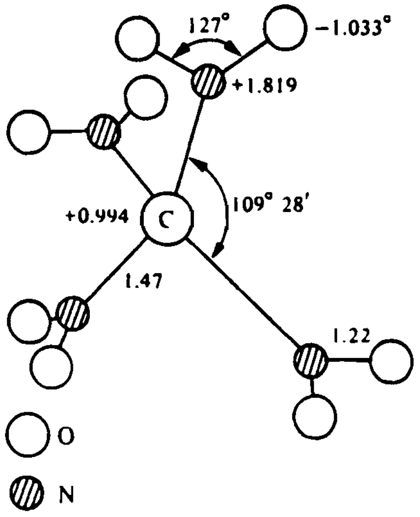


FIG. 36. Structure of tetranitromethane [156].

Chemical Properties (Vol. 1, p. 589)

The most important and unique property of TNM is the perfect symmetry of the compound, absence of polarity and identical properties of all four nitro groups.

The perfect identity of the four NO_2 groups was confirmed by T. Urbański and his co-workers [260] by the simple reaction of nitryl chloride (NO_2Cl) on nitroform or its silver and potassium salts

$$(O_2N)_3C^- \; M^+ + NO_2^+ \rightarrow C(NO_2)_4 + M^+ \qquad \textbf{(43a)}$$

Potassium salt (M^+ is K^+) gives a quantitative yield of tetranitromethane.

In spite of its symmetry TNM can yield the nitronium cation NO_2^+ and trinitromethly anion $C(NO_2)_3^-$ under certain conditions. Also the existence of corresponding ionic pairs is possible as well as the formation of radicals $NO_2^{\cdot}$ and $C(NO_2)_3^{\cdot}$.

As a rich compound of NO_2 groups, TNM shows strong electron accepting properties and several complexes of charge–transfer character are known which can further react to yield nitroaryls, arylnitroalkenes, α-nitroketones, tetranitroalkanes and dinitroisoxazolidines.

Perekalin and co-workers [156, 166, 167] subjected a number of charge–transfer complexes formed by TNM to a systematic study using electronic spectroscopy.

Charge–transfer complexes of TNM with unsaturated compounds are particularly characteristic: an intense colour (from yellow to dark red) can detect the presence of double bonds, for example in tautomeric forms (reaction of Ostromyslenskii [168] and Werner [169]). The reaction however, has a limited application, for example, no colour is given by maleic and fumaric acids. Also some compounds without double bonds give the colour. Such are compounds with divalent sulphur. TNM can be applied successfully to detect components in chromatograms.

Most complexes of TNM with unsaturated compounds are weak [170], their enthalpy of formation is of the order of 1.0 kcal/mol.

Perekalin, Altukhov and co-workers carried out an extensive research on addition of tetranitromethane to double bond [255–258].

Altukhov and Perekalin [156] suggested the scheme for the formation of CT complexes between TNM and a donor D:

$$D + C(NO_2)_4 \rightleftharpoons \underset{\text{Transition form}}{D^{+\delta}\cdots{}^{-\delta}C(NO_2)_4} \rightleftharpoons \underset{\text{Complex}}{[D\cdots NO_2]^{+\delta}\cdots{}^{-\delta}C(NO_2)_3} \qquad (44)$$

Nucleophilic Substitution

Hantzsch and Rinkenberger [171] established that TNM can quantitatively be hydrolysed to trinitromethane by potassium hydroxide or potassium ethoxide. However, aqueous concentrated KOH can produce a deeper hydrolysis with the formation of KNO_3, KNO_2 and K_2CO_3 [172]. The reaction of the formation of trinitromethane ('nitroform') from TNM became a standard method of making nitroform used for synthesis of polynitro aliphatic compounds.

TNM reacts with 3–5% aqueous Na_2SO_3 solution [173] (Vol. I, p. 589) and the reaction became the standard method of removing TNM from TNT.

An important reaction is that of halogenides of potassium, rubidium and caesium in dimethyl formamide yielding halogenotrinitromethane [174, 175]:

$$C(NO_2)_4 \xrightarrow[-KNO_2]{KX} XC(NO_2)_3 \qquad (45)$$

$$X = Cl, Br, F$$

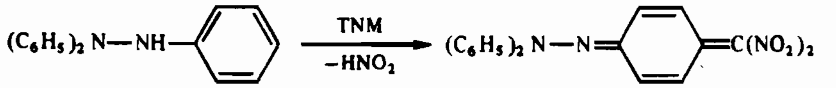
A similar chlorination can be carried out by chloramines [176].

Nitrosation of Tertiary Amines

Schmidt and co-workers [172, 177] obtained *N*-nitroso derivatives of tertiary amines by acting with TNM on the amines in pyridine or in acetic acid.

gem-Dinitromethylation

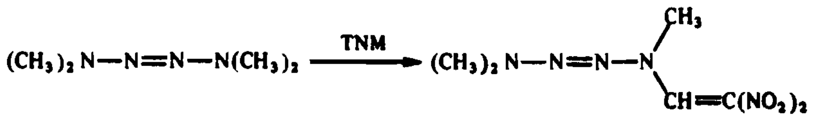
TNM in the presence of oxidizing agents can introduce gem-dinitromethyl group, for example, triphenylhydrazine and diphenylhydrazine can react according to scheme (46) [178] and (47) [179]:



(46)

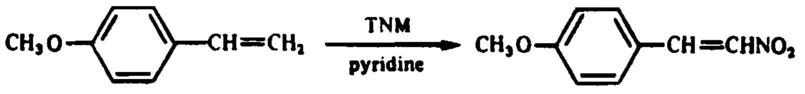
$$(C_6H_5)_2N-NH_2 \xrightarrow[-HNO_2]{TNM} (C_6H_5)_2N-N{=}C(NO_2)_2 \qquad (47)$$

An interesting reaction was reported on the action of TNM on tetramethyltetrazen [180] (48):

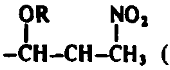

(48)

Nitration

TNM is a nitrating agent in alkaline medium. Schmidt and co-workers [181] succeeded in nitrating compounds such as arylalkanes with the double bond conjugated with those of the aromatic ring (49)


(49)

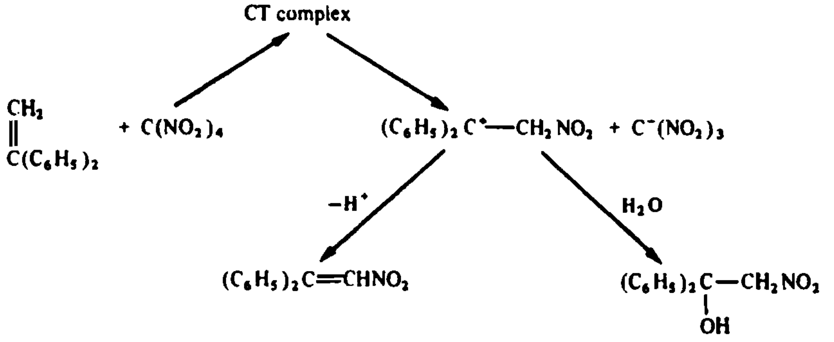
In the presence of methanol and ethanol the reaction leads to the formation of α-methoxy- and ethoxy β-nitro compounds:


$-\overset{\text{OR}}{\overset{|}{\text{C}}}\text{H}-\text{CH}-\overset{\text{NO}_2}{\overset{|}{\text{C}}}\text{H}_3$ (R = CH_3 and C_2H_5 respectively).

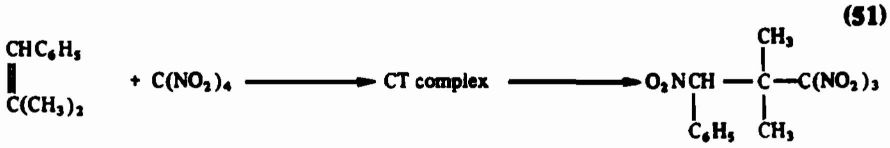
It is important to note that non-conjugated aralkenes are not nitrated with TNM.

An important contribution to the reaction of TNM with alkenes, aralkenes and dienes was given by Altukhov and Perekalin [156]. As an example the reaction of 1,1-diphenylethylene with TNM is given.

Here originally a CT complex was formed, TNM being an acceptor and the alkene a donor, next an ionic pair and the cation can react forming nitroalkene or nitroalcohol. The anion yielded nitroform (50).


(50)

Nitroalkenes react in a different way owing to the presence of a strong acceptor:


(51)

Recently thebain was nitrated with TNM in methanol [182].

Radical Reactions

A number of papers have been dedicated to homolytic degradation of TNM under the action of ultraviolet or γ-rays. The reaction of TNM with bases (e.g. benzidine) beings with the formation of CT complexes [183] yielding radical–anions which in turn are split into radicals (NO_2) and anions (e.g. nitroformanion).

Irradiation with γ-rays at 77K yielded radicals: $\cdot NO_2$ and $\cdot C(NO_2)_3$ [184].

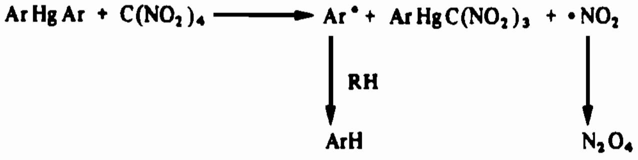
As most nitro compounds TNT inhibits polymerization induced by radiation [185, 186] and free radical polymerization [180–191]. This is rationalized by the fact that TNM is a radicals acceptor. The higher the number of nitro groups in nitro alkanes the stronger the inhibition of polymerization [189].

Ionic Polymerization

TNM is a strong acceptor of electrons and subsequently can initiate ionic polymerization. As an example it can serve the polymerization of vinylcarbazol in the presence of methyl methacrylate [192].

Metalorganic Compounds

The reaction of TNM with aryl mercury or tin compounds yielded hydrocarbons [193], for example (52):

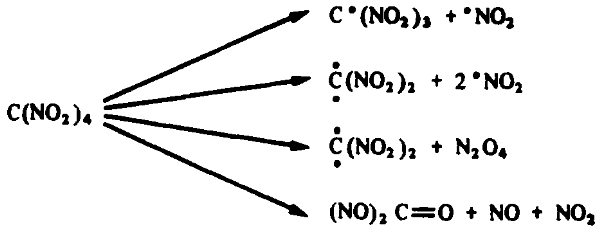

(52)

TNM reacts with copper to yield free radicals $\cdot C(NO_2)_3$ and $\cdot NO_2$ [194].

Explosive Properties

According to Roth (Vol. I, p. 590) TNM can be detonated [195] by using a strong booster of 10.5 g PETN. In a steel tube 21/27 mm diameter it gave 6400 m/s. The heat of detonation was found to be 540 kcal/kg [157]. As in most explosives with a high positive oxygen balance the addition of a small amount of organic substances to TNM considerably increases the ease of detonation.

Thermal decomposition of TNM was studied by Nazin and co-workers [196], and is depicted by scheme (53):



(53)

Toxicity (Vol. I, p. 593)

TNM is highly toxic affecting respiratory organs and the nervous system. According to the American Industrial Hygiene Association [197] the permitted concentration in air is 0.001 mg/l. A considerable number of papers have been published on the toxicity and pharmacology of TNM [198–203].

In connection with the health problem a number of physico-chemical methods for the determination of TNM in air and in solutions have been described, such as spectrophotometry, colorimetry of solutions and polarography. They are reviewed by Altukhov and Perekalin [156].

Preparation of TNM (Vol. I, p. 594)

Nitration of acetylene in the presence of mercuric nitrate seems to be the most common method of preparation of TNM. It means that the reaction is not stopped at the stage of the formation of nitroform [144] but the latter is further nitrated under the action of the excess of nitric acid.

According to Meyer [157] the best method of making TNM consists of the nitration of ketene by introducing a stream of it into cold 100% nitric acid. After the reaction is completed the resulting solution is poured into water and ice, and TNM is separated. This method was described by Darzens and G. Levy [204].

HEXANITROETHANE (HNE) (Vol. I, p. 596)

Interest has recently been revived in hexanitroethane and some data on the properties of the substance have been collected by Meyer [66], viz.:

m.p. 147°C
density 1.85 g/cm^3, ignition point 175°C

heat of explosion 743 kcal/kg
volume of detonation gases 672 l/kg
Vapour pressure: at 20°C 0.5 millibar
50°C 1.5 millibar
70°C 5.0 millibar
85°C 28.0 millibar

Physico-chemical properties were given by P. Noble and co-workers [239], the oxidizer properties by Frankel and co-workers [240], and heat of formation by Apin, Pepekin and co-workers [241]. The standard enthalpy of formation was found to be 20.0 ± 1.0 kcal/mol, and in the gas phase 36.9 ± 1.4 kcal/mol. The enthalpy of sublimation is 16.9 ± 0.4 kcal/mol.

An important finding has been described by Krien, Licht and Trimborn [242], who discovered that HNE changes its crystalline structure at around 16–19°C. The low temperature modification is stable in the range from −83° to +16°C. The low temperature form is rhombic and has density 2.21 g/cm^3 whereas that of ambient temperature is cubic and possesses the density given above (1.85). The transition is reversible and the heat of transition $-\Delta H$ is 9.87 cal/kg. Specific heat at 16°C is 0.26 kcal/kg.

It was found [242] on a differential scanning calorimeter that the endothermic crystal change begins at +17°C, sublimation at +127°C followed by exothermic decomposition (142°C) and endothermic melting at 147°C.

The substance has a waxy appearance and can be readily pressed but at 0°C and below that temperature some cracks can appear due to the change of the crystal habit.

Thermal decomposition of HNE was studied by H. P. Marshall and co-workers [243], Nazin, Manelis and Dubovitskii [244]. They gave the following values for the energy of activation: $E = 37.8$ kcal/mol and log B = 18.5 [243] and 35.8 kcal/mol and log B = 17.3 (for the interval of temperatures 90–135°C) [244].

NITROCARBOXYLIC ACIDS

Nitrocarboxylic acids were reviewed by Novikov and co-workers in their rich monograph [9]. Although not possessing explosive properties they may be of value for the synthesis of amino acids, surface active agents and ingredients of rocket propellants.

Only a brief outline will be given here, the reader should otherwise consult the monograph [9].

Nitration of fatty acids was first effected by Bous in 1855 [205] who nitrated caprylic acid with nitric acid. Claus and Pfeiffer [206] nitrated stearic acid with nitric acid (d 1.48) in glacial acetic at the solutions boiling temperature. In the search for an industrial application for the nitrated saponifiable oils, Radcliffe and Polychronis [207] nitrated stearic, hydroxystearic, oleic and ricinoleic acids. They found that cold nitric acid had no effect on stearic acid, whereas oleic acid (as should be expected from its unsaturated character) yields nitro-oleic acid along with oleic acid nitrate. Ricinoleic acid in turn gave on nitration nitro-nitrate and nitrate derivatives.

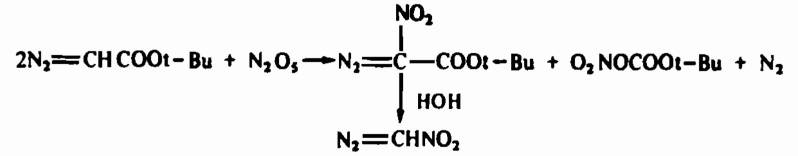
T. Urbański and Biernacki [208] nitrated ethyl *n*-valerate with nitric acid in glacial acetic acid–acetic anhydride at 23 ± 2°C and found that a mixture of 2-, 3- and 4-nitrovalerates was formed in the ratio 0.5:0.7:1. At 63 ± 2°C a certain amount of 1-nitrobutane was formed due to the decarboxylation of the 2-nitrovalerate.

Valeric acid was not nitrated at 23°C and required a minimum temperature of 33 ± 2°C.

The nitration of propionic acid with nitric acid in the vapour phase gave a small yield (5%) of 3-nitropropionic acid according to Hass and Hudgin [209].

NITRODIAZOMETHANES

Interesting nitro derivatives of diazomethane were obtained by Schöllkopf and co-workers. Thus Schöllkopf and Markusch [210] described nitrodiazomethane which was obtained from *t*-butyl diazoacetic ester by nitration with N_2O_5 followed by hydrolysis (54) *see* also Chapter I, p. 30:



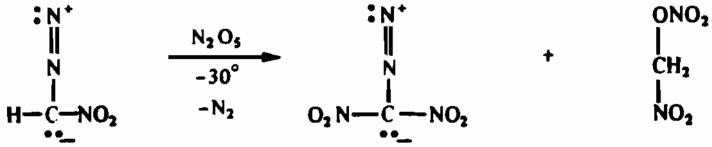
$$2N_2{=}CHCOOt\text{-}Bu + N_2O_5 \longrightarrow N_2{=}\overset{NO_2}{\overset{|}{C}}\text{—}COOt\text{-}Bu + O_2NOCOOt\text{-}Bu + N_2 \qquad (54)$$

$$\xrightarrow{HOH} N_2{=}CHNO_2$$

m.p. 55°C

Nitrodiazomethane decomposes with HCl in moist ether yielding $ClCH_2NO_2$.

Dinitrodiazomethane was prepared by the action of nitric anhydride on mononitrodiazomethane [211] (55):



$$H\text{—}\underset{\bullet\bullet -}{C}(\text{—}N{=}\ddot{N}^+)\text{—}NO_2 \xrightarrow[-N_2]{N_2O_5,\ -30^\circ} O_2N\text{—}\underset{\bullet\bullet -}{C}(\text{—}N{=}\ddot{N}^+)\text{—}NO_2 + O_2NO\text{—}CH_2\text{—}NO_2 \qquad (55)$$

Dinitrodiazomethane
m.p. 65°C d.
42%

No data on explosive properties are available. It appears that the low decomposition temperature renders the compounds of no practical use, but they are certainly of great theoretical interest.

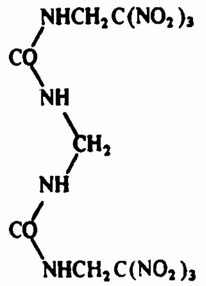
NITRO DERIVATIVES OF UREA

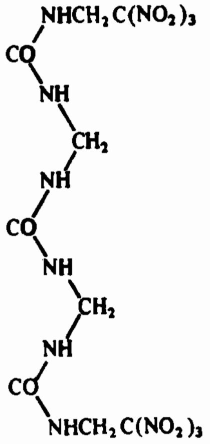
N,N-bis (β,β,β)-Trinitroethyl Urea (IV), p. 247

This interesting substance was obtained by Wetterholm [250] in 1951 by reaction (56):

$$2(NO_2)_3C\,CH_2OH + NH_2CONH_2 \longrightarrow (NO_2)_3C\,CH_2NH\,CO\,NH\,CH_2C\,(NO_2)_3 \quad (56)$$

DiTeU separated as a white precipitate sparingly soluble in water. Another method consists in reacting dimethylolurea with nitroform [251]. The product is not a single compound: it contains less soluble fractions of di- and trimer, which can be removed by crystallization:





The pure DiTeU has a favourable oxygen balance:

$$C_5H_6O_{13}N_8 \longrightarrow 5\,CO_2 + 3\,H_2O + 4\,N_2. \quad (57)$$

The explosion enthalpy is 1645 kcal/kg.

The deflagration point is 210°C, the rate of detonation 8000 m/s at density 1.62, lead block 465 cm^3. It is less sensitive to impact than RDX.

A pilot plant for DiTeU, producing 30 kg/hr DiTeU, exists in Sweden at Nitro-Nobel A.G. A great advantage of the production is that no spent acid is formed.

NITROSO COMPOUNDS (Vol. I, p. 602)

Nitro-nitroso Alkanes ('Pseudonitroles')

As is known, pseudonitroles are formed by nitrosation of secondary nitroalkanes. Very little interest has been shown to this class of compounds which have been known since the classical work of Victor Meyer in 1873. For early work see [7].

More recently the mechanism for the formation of pseudonitroles and their stereo chemistry has been examined by Noland and Libers [212]. The pseudonitroles can be oxidized to gem-dinitro compounds with air or hydrogen peroxide.

Recently de Boer and Bolsman [213] examined photolysis of 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen and came to the conclusion that a homolytic fission of C—NO bond occurred at 40°C and generated a radical pair: NO and α-nitrocyclohexyl, Solvolysis occurred in different solvents. In benzene, cyclohexanone was formed as a major product and small amounts of 1,1-dinitrocyclohexane, as well as 1-nitrocyclohexene and nitrocyclohexane.

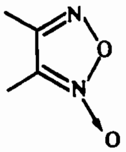
'Hexanitrosobenzene'

As mentioned in Vol. 1, p. 603, hexanitrosobenzene now has the accepted structure of 'Benzotrisfuroxane'.

This was confirmed by several physico-chemical methods, such as:

X-ray diffraction [215],
X-ray photoelectron spectroscopy [216],
Vibrational spectroscopy [217],
Laser-Raman study [218],
Nitrogen NMR [219],
Carbon-13 NMR [220].

It should also be pointed out that the substances with a furoxane structure (VII):



VII

possess explosive properties [221–225].

An excellent review on furoxanes has been given by Kaufman and Picard [226].

Nitroenamines

Enamines are an interesting group of compounds, for example VIII

$$(CH_3)_2N\ CH = CH\ NO_2$$

VIII

An excellent review has recently been given by Rajappa [229]. The substances and their properties are outside the scope of the present book.

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APPENDIX

Nitromethane – Aluminium Chloride Complex

Závada, Pankova and Z. Arnold [1] described a complex of nitromethane with aluminium chloride which is a convenient form of the Friedel-Crafts catalyst [2].

Substituted Nitro Alkanes

Thermal decomposition. A considerable number of substituted nitroalkanes were prepared by Soviet chemists and their thermal decomposition was examined by Nazin and coworkers [3, 4] in view of determining their activation energy and frequency factor. Some of the results are collected in Table A1 and in a summarizing review of Nazin and Manelis [5]

TABLE A1. Energy of activation of thermal decomposition of di- and tri-nitroalkanes and their halogen derivatives

Compound	Temperature range °C	Activation energy kcal/mol	Frequency factor log B	References
CH_3NO_2	360-390	54.3	14.3	[3]
$CH_3CH(NO_2)_2$	197-227	47.1	16.7	[4a]
$CH_3CH_2CH(NO_2)_2$	215-265	48.0	16.9	
$CH_3(CH_2)_2CH(NO_2)_2$	219-244	48.2	17.0	
$C(NO_2)_4$	86 177	38.2	16.3	[4b]
$CF(NO_2)_3$	178-236	41.9	15.4	
$CCl(NO_2)_3$	120-165	36.4	15.75	
$CH(NO_2)_3$	180-200	42.4	15.9	[4c]
$CHCl(NO_2)_2$	180-200	40.6	16.1	
$CF_2(NO_2)_2$	235-270	47.4	15.9	[4d]
$CH_3CF(NO_2)_2$	214-262	47.7	17.0	
$C(NO_2)_3-C(NO_2)_3$	90-135	35.8	17.3	
$CF(NO_2)_2-C(NO_2)_3$	88-140	36.5	17.3	
$CF(NO_2)_2-CF(NO_2)_2$	107-180	42.2	18.0	
$CH_3C(NO_2)_3$	160-200	43.2	17.2	[4e]

Thermochemical properties. A monograph should be mentioned of thermochemistry of nitro compounds by Lebedev and co-workers [9]. Pepekin and co-workers examined the enthalpy of formation of dinitrophenylmethane, trinitrophenylethane fluordinitrophenylmethane [6], and fluordinitromethane [7]. The results are given in Table A2.

TABLE A2. Thermochemical data of some nitroalkane derivatives

Compounds	Enthalpy of formation in gas-phase kcal/mol	Energy of the bond C–C between phenyl or benzyl and $C(NO_2)_2$ or $C(NO_2)_3$ kcal/mol
$C_6H_5CH(NO_2)_2$	8.3	100.2
$C_6H_5CH_2C(NO_2)_3$	15.7	79.1
$C_6H_5C\,F(NO_2)_2$	−44.2	105.1
$CH\,F(NO_2)_2$	−56.1	–

Steric Effects in Nitroalkanes

Novikov and co-workers [8] studied steric effects in mono- and polynitroalkanes. They calculated the equilibrium of configuration, energy of strains and enthalpy of atomization. Steric effects from the nitro groups increase with the increase of their number and the increase of the length of the alkyl chain.

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CHAPTER 9

DIFLUOROAMINO COMPOUNDS

As a result of searching for new explosives and in particular rocket propellants, a new group of explosives was found – that of organic compounds containing difluoroamino group – NF_2. The group can also be regarded as a modification of the nitro group, where two atoms of oxygen were replaced by atoms of fluorine.

There is now extensive patent literature covering the preparation of difluoroamino compounds and describing their potential use as high-energy propellant ingredients. However, some of the compounds possess properties which cast doubt on the safety of their preparation and handling. A striking example is the simplest member of the family with difluoroamino group, i.e. difluoroamine (NHF_2). This is a particularly dangerous compound: unexpected detonations have been reported.

It appears that interest in difluoroamino compounds is now diminishing, as far as their application as explosives is concerned. Nevertheless the chemistry of difluoroamino compounds remains very interesting.

Two routes for the preparation of difluoroamino compounds are known:

(1) through the direct fluorination of amines,
(2) through the reactions with tetrafluorohydrazine, accompanied by thermal or photochemical dissociation of this compound.

A review of the work on derivatives of nitrogen fluoride compounds including those with difluoroamino group was given by J. K. Ruff [1]. Fokin and Kozyrev [30] published an extensive review dedicated to difluoroamino compounds.

Reviews on difluoroamino compounds appeared also in Advances in Chemistry Series of American Chemical Society [34]. They were reviewed mainly for their application as rocket propellants.

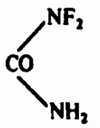
DIRECT FLUORINATION OF NON-AROMATIC COMPOUNDS

Although the first compounds with NF_2 group were obtained as early as 1936 by O. Ruff and Giese [35] the most important work started relatively recently in the early sixties. These were the indications of the possible transformation of NH_2 into NF_2 given by Lawton and co-workers [2] and Grakauskas [3].

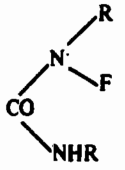
Direct Fluorination of NH_2 and NH Groups in Aliphatic Compounds

Lawton acted on solid urea with fluorine diluted with nitrogen at 0°C and among a variety of compounds isolated a solid substance which proved to be identical with that prepared by Grakauskas [3] through the action on urea in aqueous solution with fluorine diluted with nitrogen at 0–5°C. It proved to be *N,N*-difluorourea (I). It was extracted with ether as a hygroscopic, lackrymatory solid, m.p. 43°C.

Additional examples of fluorination of compounds containing NH_2, $NHCH_3$ or NHC_2H_5 groups in an aqueous medium were later also reported [4]. They described the formation of such compounds as II–IV.

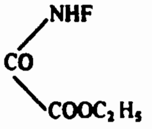


I



II

$R = CH_3, C_2H_5$



III

CH_3NF_2

IV

A compound analogous to I with SO_2 group instead of CO was prepared by fluorination of sulphonamide: $NH_2SO_2NF_2$ [5].

Difluoramine (Difluorimide) NHF_2

Difluoroamine NHF_2 was prepared by decomposition of I or III.

Difluoramine is a gaseous substance [6] with m.p. −116.4 to −117.1°C, b.p. −23.6, density $d = 1.424 - 0.00202\,t$ (d measured at −42.5°C was 1.513). It possesses extraordinary explosive properties, being extremely sensitive to impact, detonating spontaneously when cooled to −196°C in liquid nitrogen. The N−F bond strength in NHF is estimated to be 72 kcal/mol [7b].

According to Lawton and Weber [6] it was formed as one of the products of the action of fluorine diluted with nitrogen (in proportion 1:4 to 1:10) on solid urea at 0°C. The resulting liquid mixture was distilled under reduced pressure and condensation at −142°C gave NHF_2 with a yield of 30% (calculated on the fluorine used). The nondistilling residue was composed of difluorourea (I).

Difluoroamine was formed from *N,N*-difluorourea through acid hydrolysis:

$$NF_2\,CO\,NH_2 \xrightarrow{H^+,\ H_2O} NH\,F_2. \qquad (1)$$

Kennedy and Colburn [7a] obtained a small quantity of difluoroamine by acting on nitrogen trifluoride with arsenic at 250–300°C. The best method of making the compound consists in hydrolysis of trityldifluoroamine with sulphuric acid. A quantitative yield was obtained [8]. Trityldifluoroamine in turn was obtained by acting with tetrafluorohydrazine on trityl cation [9]:

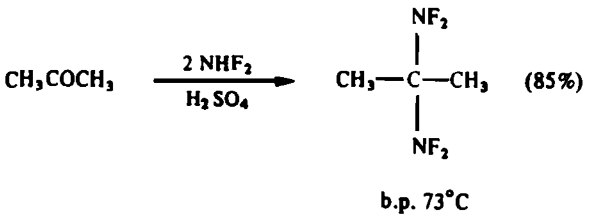
$$N_2F_4 + (C_6H_5)_3C^+ \longrightarrow \underset{\text{m.p. } 75\text{-}77^\circ C}{(C_6H_5)_3CNF_2} \xrightarrow{H_2SO_4} NHF_2 \qquad (2)$$

Difluoroamine hydrolysed under the action of bases and fluorine anion was evolved [10].

Difluoroamine forms complexes with ethers and Lewis acids, and decomposes on contact with copper, stainless steel and some organic compounds, such as urea [6].

It reacts with carbonium ions to yield *N,N*-difluoroamines [11].

Difluoroamine reacts with carbonyl compounds in acid medium to yield difluoroamino derivatives [12a], for example:



$$CH_3COCH_3 \xrightarrow[H_2SO_4]{2\,NHF_2} \underset{\text{b.p. } 73^\circ C}{CH_3-\overset{NF_2}{\underset{NF_2}{C}}-CH_3} \quad (85\%) \qquad (3)$$

and with acetylenes to yield NF_2 substituted olefins [12b].

No explosive properties of such substances were reported.

Other Non-aromatic Difluoroamines

Sharts [13] fluorinated a number of aliphatic amines.

He fluorinated hexamethylenediamine with a fluorine-nitrogen mixture (1:2) in aqueous medium in the presence of sodium bicarbonate, trichlorofluoromethane and methylene dichloride at temperatures below 2°C.

N,N,N^1,*N*^{1}-Tetrafluorohexamethylenediamine or 1,6-bis(difluoroamino)hexane (b.p. 70–75°C at 0.1 mmHg) resulted with a yield of 23%.

In a similar manner cyclohexylamine was converted into *N.N*-Difluorocyclohexylamine (the yield was 66%, based on cyclohexylamine and 23% on fluorine). It is a liquid boiling over the range 69–81°C under 80–90 mmHg.

Davis and Graves [14] fluorinated guanidine and obtained an explosive product: perfluoroguanidine $NF = C(NF_2)_2$. Rosenfeld and co-workers [15] fluorinated cyanoguanidine and obtained three major products V–VII:

$CF(NF_2)_3$

V

$$F_2N\underset{\underset{NF}{\|}}{C}NFCF_2NF_2$$

VI

$(F_2N)_2CFNFCF_2NF_2$

VII

Compounds VI (b.p. 55°C) and VII (b.p. 60°C) possess explosive characteristics.

FLUORINATION OF NITROAROMATIC AMINES

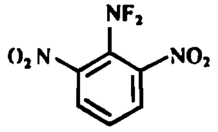
Coon and co-workers [16] have found a general synthetic procedure for the preparation of nitroaromatic difluoramines. Nitroaromatic monoamines, such as picramide and its analogues have been converted in high yield into the corresponding difluoramines in liquid hydrogen fluoride and in some cases in organic solvents, such as acetonitrile, by using fluorine diluted with nitrogen, at temperatures below 0°C.

Nitroaromatic diamines and triamines undergo similar fluorination reactions.

Dinitroanilines were fluorinated in good yield, but fluorination of non-nitrated amines (such as aniline) is accompanied by ring fluorination *ortho* to the NF_2 group.

According to the same authors the reaction of fluorination occurs through a radical mechanism.

All substances described below possess marked explosive characteristics [16].



VIII

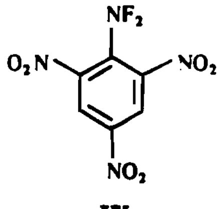
1-Difluoramino-2,6-dinitrobenzene (VIII)

This substance forms light yellow coloured needles (from 50/50 chloroform/hexane), m.p. 91–93°C.

It was obtained by fluorination of 2,6-dinitroaniline in acetonitrile at −10 to −5°C with a stream of 15% fluorine in nitrogen. The yield was *ca.* 60%.

1-Difluoroamino-2,4-dinitrobenzene

This substance was not isolated in a pure form. The liquid product of fluorination of 2,4-dinitroaniline contained 1-difluoroamino-6-fluoro-2,4-dinitrobenzene.

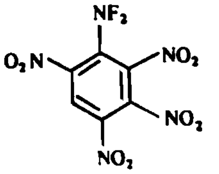


IX

1-Difluoroamino-2,4,6-trinitrobenzene (IX)

The substance forms light yellow coloured crystals, m.p. 69°C.

As mentioned already it was obtained by fluorinating 2,4,6-trinitroaniline dissolved in anhydrous hydrogen fluoride at −5° to 0°C with a stream of 60% fluorine in nitrogen. The yield was 75%.



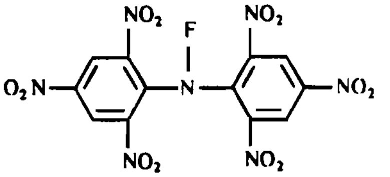
X

1-Difluoroamino-2,3,4,6-tetranitrobenzene (X)

The substance forms yellow coloured crystalline solids, m.p. 84°C.

It was obtained [16] from tetranitroaniline (Vol. I, p. 560) in the same way as 1-difluoramino-2,4,6-trinitrobenzene, the only difference being that no external cooling was used and the temperature in the course of fluorination was that of the b.p. of anhydrous hydrogen fluoride (+19°C). The yield was 75%.

Difluoraminopentanitrobenzene was obtained by fluorinating pentanitroaniline (Vol. I, p. 562) in the same way as fluorination of picramide, the only difference was that no external cooling was applied. The product was stable only in solution and could be detected by NMR spectrum. In the solid state – the orange coloured crystals decomposed quickly and formed viscous oil.

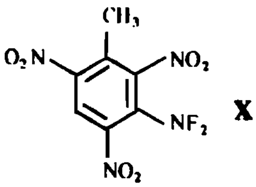


XI

Hexanitrodiphenylfluoramine (XI)

This is a crystalline, orange coloured solid, m.p. 102–105°C.

It was made from hexanitrodiphenylamine in acetonitrile solution by fluorinating with 15% fluorine at temperatures of −10 to −5°C (54% yield). It decomposed at room temperature within a few days and is stable only below −18°C.



XII

3-Difluoramine-2,4,6-trinitrotoluene (XII)

This substance forms yellow coloured crystalline solids, m.p. 111°C.

It was obtained in the same way as (IX) at −16 to −4°C with 46% fluorine–nitrogen. The yield was 78%.

Other Difluoramino Nitroaromatics

The following difluoramino nitroaromatics were also prepared [16]:

a. 3-Difluoramino-2,4,6-trinitroanisol, a yellow coloured liquid,
b. 3,5-bis(difluoramino)-2,4,6-trinitrotoluene, yellow coloured crystals m.p. 143–145°C,
c. 3-difluoramino-5-chloro-2,4,6-trinitrotoluene, yellow coloured crystals, m.p. 149–153°C,
d. 1,5-bis(difluoramino)-2,4-dinitrobenzene,
e. 1,5-bis(difluoramino)-2,4-dinitro-6-fluorobenzene. Compounds (d) and (e) were obtained in a mixture by fluorinating 1,5-diamino-2,4-dinitrobenzene.
f. 1,3,5-tris(difluoramino)-2,4-dinitrobenzene, light yellow coloured crystals, m.p. 54–56°C.

The latter was obtained in the course of fluorination of 1,3,5-triamino-2,4-dinitrobenzene along with 1,3,5-tris(difluoramino)-2,4-dinitro-1,2,3,4,5,6-hexafluorocyclohexane – a liquid product which was formed from the saturation of the benzene ring of the product (f) with fluorine.

No reference to their explosive properties was given, but private information is that they do not differ from the mother nitro compounds.

FLUORINATION THROUGH THE ADDITION OF TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine NF_2-NF_2

Tetrafluorohydrazine is a gaseous substance with b.p. −73°C.

The preparation of tetrafluorohydrazine was in a way a turning point in the chemistry of difluoroamino compounds by offering a stable reactive substance which could also yield NF_2 free radicals. The enthalpy of dissociation (4)

$$N_2F_4 \longrightarrow 2\cdot NF_2 \tag{4}$$

is very low 20 ± 1 kcal/mol [1].

Tetrafluorohydrazine was obtained by Colburn and Kennedy [17] by passing nitrogen trifluoride over copper at 375°C:

$$2\,NF_3 + Cu \longrightarrow N_2F_4 + CuF_2. \tag{5}$$

The reaction can also be carried out with other metals, such as Fe, As, Sb and Bi. The conversion was 42–62% and the yield 62–71%.

(Nitrogen trifluoride was obtained by O. Ruff and co-workers [18] through electrolysis at 125°C of molten ammonium hydrogen fluoride: $NH_4F.HF$. It is a stable, gaseous, b.p. −119°C, substance which can be hydrolysed by hot water vapour.)

It was also reported that nitrogen trifluoride could be obtained by reacting N_2O with fluorine at 700°C [19].

On other methods of preparation of tetrafluorohydrazine – see [1].

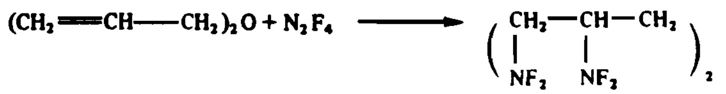
Reactivity of Tetrafluorohydrazine

Frazer [20] has shown that tetrafluorohydrazine can react with methyl and ethyl iodide in a light initiated reaction to give *N,N*-difluoroaminomethane and ethane respectively.

A number of authors reported the formation of bis(difluoroamino) compounds by the addition of tetrafluorohydrazine to unsaturated aliphatic and aromatic compounds [21–26].

According to Cerfontain [24] tetrafluorohydrazine can react with polycyclic aromatic hydrocarbons in iso-octane as a solvent at 40°C. Thus anthracene yielded 9,10-bisfluoroamino-9,10-dihydroanthracene. The product does not show good stability, it decomposed above 130°C with a gas evolution and at 220°C yielded mainly the parent hydrocarbon. Similarly the product of the reaction of stilbene with tetrafluorohydrazine (which was 1,2-bisdifluoroamino-1,2-diphenylethane) decomposed above 80°C.

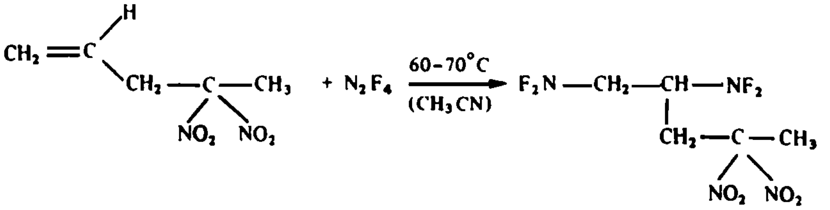
The reaction of tetrafluorohydrazine with diallyl ether was studied by Reed [26]. The main product of the reaction (48%) was di[2,3-bis(difluoroamino) propyl] ether (6)



$$(CH_2{=}CH{-}CH_2)_2O + N_2F_4 \longrightarrow \left(\begin{array}{lll}CH_2 & -CH & -CH_2\\ | & \ | & \\ NF_2 & \ NF_2 & \end{array}\right)_2 \qquad (6)$$

The other products were tetrahydrofurane derivatives.

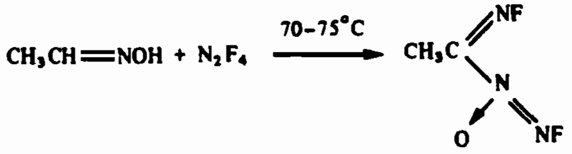
Fokin and co-workers [32] described interesting reactions of nitroalkenes with tetrafluorohydrazine. Such was the reaction of 2,2-dinitropentene-4 with tetrafluorohydrazine yielding 2,2-dinitro-4,5-bis(difluoroamino)-pentane (7) with a yield of *ca*. 36%:



(7)

The reaction is very solvent dependent. Decomposition occurred in most solvents but the best proved to be acetonitrile.

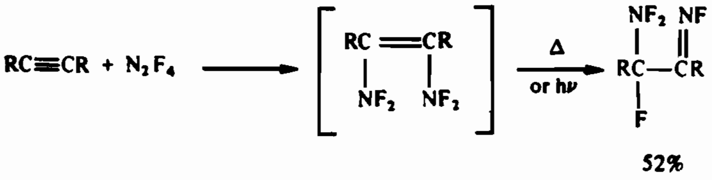
Fokin and co-workers [33] studied reactions of oximes with tetrafluorohydrazine, for example (8)



(8)

Most of the latter products are unstable. The only stable compounds were obtained from aromatic oximes.

The addition of N_2F_4 to acetylenes was studied by a number of authors [27, 28]. The reactions give ethylene derivatives unstable and readily isomerizing on further heating or under the influence of irradiation (9)



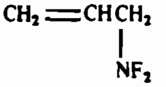
(9)

The fact that NF_2 radical formed through the equilibrium $N_2F_4 \rightleftharpoons 2{\cdot}NF$ absorbs at 260 mn suggests that it possesses photochemical properties. Indeed it was found that the irradiation of methane with N_2F_4 produced difluoroaminomethane (10)

$$CH_4 \xrightarrow[h\nu]{N_2F_4} CH_3NF_2 + HCN \qquad (10)$$

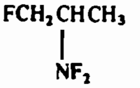
Similarly ethane yielded difluoroaminoethane $C_2H_5NF_2$ and CH_3CN.

Olefins also reacted with N_2F_4 under irradiation, for example propylene yielded 50% of a mixture of substituted propylene and propane (XIII–XI) [29]



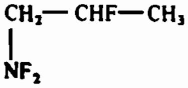
$CH_2{=}CHCH_2NF_2$

XIII



$FCH_2CH(NF_2)CH_3$

XIV



$CH_2(NF_2){-}CHF{-}CH_3$

XV

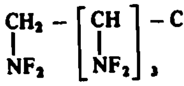
EXPLOSIVE PROPERTIES OF DIFLUOROAMINOALKANES AND ALKENES

A few experimental data of explosive properties of difluoroaminoalkanes and alkenes were collected and theoretical calculation of their properties was given by Pepekin [31].

According to Berke and associates [43] bis-difluoroaminopropane and -butane give the rates of detonation:

$C_3H_6N_2F_4$, $\rho = 1.26$, $D = 6300$ m/s,
$C_4H_8N_2F_4$, $\rho = 1.20$, $D = 6000$ m/s.

Voskoboynikov and co-workers [44] have found similar figures for bis-difluoroaminobutane and -pentene. They also described an interesting compound: tetra-difluoroaminopentane:



$$\underset{NF_2}{\underset{|}{CH_2}} - \left[\underset{NF_2}{\underset{|}{CH}}\right]_3 - CH_3, \quad \rho = 1.51, D = 7000 \text{ m/s}.$$

The general conclusion is that compounds with NF_2 group show similar explosive properties as those with the same number of NO_2 groups.

Theoretical Aspects of Properties of NF_2 Compounds

A series of theoretical papers on the difluoroamino group and compounds have appeared. Their aim was to find a theoretical background for the use of difluoroamino compounds in propellants.

1. Isotopic exchange reaction of difluoroamine (NF_2H) with D_2O and trifluoro deutero acetic acid (CF_3COOD) was examined by Becker and Impastato [36].

2. The reaction of difluoroamine with Lewis Acids [37].

3. A general paper on the chemistry of difluoroamines by Craig *et al.* [38] was also published. It was dedicated to understanding the nature of N–F and N–X bonds and to obtain a picture of the relative electron distribution in X–NF_2 compounds, where X = F, Cl, H, NF_2, CH_3, C_2H_5 and CF_3. The electron affinity of cation NF_2^+ was found to be very high and by adding an electron, a relatively stable radical NF_2 was favoured. The electron distribution is more symmetrical than in anion NF_2^- and cation NF_2^+ which do not seem to be sufficiently stable.

4. In searching for high energy explosives the reactions were examined between difluoroamino compounds and

(a) organometallic compounds,
(b) nitric acid [39]. A variety of compounds were obtained in both instances, such as:
(a) azo-compounds, dialkyldifluoro-hydrazine, tertiary amine and hydrocarbon,
(b) alkyl nitrates and nitrites.

5. Reactivity of nitrogen fluorides NF_3, N_2F_4 and cis- and trans-N_2F_2 was examined by Hurst and Khayat [40]. Nitrogen trifluoride (NF_3) is inert to pure

water but reacted with aqueous bases at 100°C to give nitrite and fluoride. N_2F_4 was hydrolysed slowly with water at 60–100°C. Cis- and trans-N_2F_2 were hydrolysed with water at 74° and 89°C respectively. The reactions were of the first order with respect to N_2F_2 and the major products are N_2 and O_2 [41].

Thermochemistry

Pepekin and Apin [42] calculated enthalpy of formation of 1,1-bis(difluoroamine)cyclohexane and the energy of the bond N–F. The enthalpy of formation – ΔH_f was found to be 52.5 kcal/mol and the thermochemical energy of the bond N–F was 68.4 cal.

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CHAPTER 10

ESTERS
NITRATE ESTERS
(*O*-NITRO COMPOUNDS)

Although nitrate esters continue to be widely used and are important explosives, their chemical properties are described to a much lesser extent than those of *C*-nitro compounds. This is understandable when considering the wide use of *C*-nitro compounds, particularly aromatic ones, not only as explosives but in a great variety of uses as intermediates and finished products. For this reason the excellent monograph of Patai, series edited by H. Feuer [1], does not contain a chapter on *O*-nitro compounds and the only review papers dedicated solely to *O*-nitro compounds were by Boschan, Merrow, Van Dolah [2] and Connon [3].

STRUCTURE (Vol. II, p. 1)

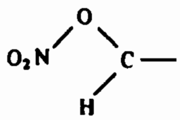
Three kinds of nitrate esters are distinguished: primary, secondary and tertiary deriving from primary, secondary and tertiary alcohols respectively:

(1) primary	CH_2-ONO_2
(2) secondary	$CH-ONO_2$
(3) tertiary	$C-ONO_2$

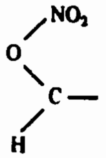
This was pointed out by T. Urbański and Witanowski (Vol. I, p. 6) who found the spectroscopic (infra red) method of distinguishing the above species which is described later in the paragraph on spectroscopy of nitrate esters.

DIPOLE MOMENTS (Vol. II, p. 3)

Recent measurements of dipole moments carried out by Lemanceau and Caire-Maurisier [4] brought some new and important conclusions to the problem of the conformation of nitroglycerine and other nitrate esters with three or four atoms of carbon in the chain. They concluded that there is less need for admitting various conformations produced by the rotation around C—C bonds of the chain $CH_2-CH-CH_2$. Instead they rationalized their results in terms of the rotation in groups $C-ONO_2$ around the bonds C—O, viz. Formulae Ia and Ib:

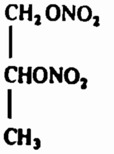


Ia



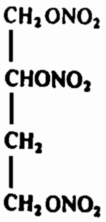
Ib

The same applies to propane-1,2-diol dinitrate (II) and butane-1,2,4-triol trinitrate (III). They also examined NMR spectra of nitrate esters – their conclusions are reported in the paragraph on NMR of nitrate esters (p. 284).



$$\begin{array}{l}\mathrm{CH_2ONO_2}\\ |\\ \mathrm{CHONO_2}\\ |\\ \mathrm{CH_3}\end{array}$$

II



$$\begin{array}{l}\mathrm{CH_2ONO_2}\\ |\\ \mathrm{CHONO_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2ONO_2}\end{array}$$

III

SPECTROSCOPY (Vol. II, p. 4).

T. Urbański and Witanowski [5] found that a stepwise substitution of hydrogen atoms with methyl groups in methyl nitrate lowers the frequency of asymmetric vibrations by about 5 cm^{-1} for each methyl introduced. Subsequently it is possible to distinguish between primary, secondary and tertiary simple alkyl nitrates by their ν_{as} as frequencies, viz.:

1632–1630,
1626,
1621 cm^{-1} respectively.

On the contrary ν_{sym} vibrations of simple nitrate esters (1283–1280 cm^{-1}) is unaffected by the substitution as above.

The fact observed by Pristera (Vol. II, p. 6) that the infra red asymmetric vibration band of *ca.* 1639 cm^{-1} of nitroglycerine has a shoulder was rationalized by Rossmy [6], T. Urbański and Witanowski (Vol. II, pp. 4, 6) as the result of rotational isomerism around the bond $\mathrm{C{-}\underset{\underset{\displaystyle ONO_2}{|}}{C}}$.

Nevertheless the shoulder can also be partly produced by the fact that the nitroglycerine molecule contains both the primary groups and the secondary *O*-nitro group. This refers also to all nitrate esters with longer chains, such as esters of erytritol and hexitols (e.g. mannitol, sorbitol), but not in esters of ethylene glycol and pentaerythritol which show a splitting of the absorption bands: [7] and (Vol. II, p. 6).

The data for infra red spectra obtained by T. Urbański and Witanowski [5, 7] were used by Czuchajowski and Kucharski [8] in the series of papers on calculation force constants. Such a theoretical approach for methyl nitrate was first given by Shlyapochnikov, Novikov and Zavilovich [9].

Czuchajowski and Kucharski examined a full range of derivatives of ethyl nitrate of the general formula $Y{-}CH_2{-}CH_2{-}ONO_2$. Table 45 gives comparative results of experimental values [5, 7] and their calculation [8]. Table 46 gives stretching force constants and the influence of +*I* inductive effect of the substituents *Y*.

TABLE 45. Stretching frequencies of NO_2 group in $Y{-}CH_2{-}CH_2{-}ONO_2$

Y	ν_{as} (NO_2) cm^{-1}		ν_s (NO_2) cm^{-1}	
	exper. [4, 6]	theor. [7]	exper. [4, 6]	theor. [7]
OH	1631	1632	1282	1284
Cl	1652 1640	1651	1280	1283
Br	1651 1641	1655	1282 1273	1284
I	1662 1640	1660	1281 1262	1284
ONO_2	1656 1643	1656	1282 1271	1273

TABLE 46. Stretching force constants in $Y{-}CH_2{-}CH_2{-}ONO_2$. Influence of +I inductive effect (according to Czuchajowski and Kucharski [7])

Y	K_{O-N}	K_{N-O}
	m dyn/A	
OH	4.40	9.04
Cl	4.10	9.25
Br	4.07	9.29
I	3.99	9.35
ONO_2	4.07	9.29

In the next paper [10] Czuchajowski and Kucharski extended their calculations of valence force field (VFF) to compounds of the general formula $Y{-}CH_2{-}CH_2{-}ONO_2$, where *Y* was NO_2, CN, ONO_2. Their calculated results included the difference between gauche and trans conformers, the values of which were 1655–1652 and 1644–1641 cm^{-1} respectively and are also in agreement with the experimental data [7].

NUCLEAR MAGNETIC RESONANCE

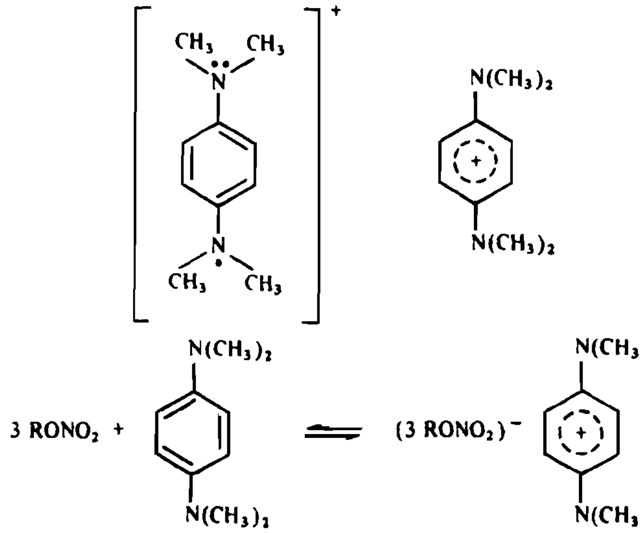
Lemanceau and Caire-Maurisier [4] examined NMR spectrum of nitroglycerine with a view to determining the conformation of the compound. The spectrum is of the type *ABCA'B'* and appears to favour the ecliptic conformation of C–ONO_2 groups.

Pobłocka, T. Urbański and Wacławek [11] examined NMR spectra of erythritol tetranitrate (an acceptor) while studying its charge–transfer complexes with bases as electron donors.

ELECTRON ATTRACTING PROPERTIES OF NITRATE ESTERS AND CHARGE–TRANSFER COMPLEXES

T. Urbański (Vol. II, pp. 167, 169) and later Witanowski [12] have shown by way of thermal analysis that some *O*-nitro compounds such as D-mannitol hexanitrate and erythritol tetranitrate can form additional complexes with aromatic nitro compounds.

In a series of papers [13–15, 22] T. Urbański, Hetnarski and Południkiewicz described charge–transfer complexes with nitrate esters as electron acceptors. Tetramethyl-*p*-phenylenediamine (TMPD) was used as an electron donor. The visible stage of the reaction between nitrate esters and TMPD in 1,2-dichloroethane as the solvent was the formation of the bluish-violet coloured radical-ion known as Wurster cation (IV) [16, 17] formed from TMPD through the loss of one electron. The presence of Wurster cation is manifested by two absorption bands in the electronic spectrum: 570 and 620 nm [17]. The authors established that at least three ONO_2 groups are needed to form one mole of IV, for example:

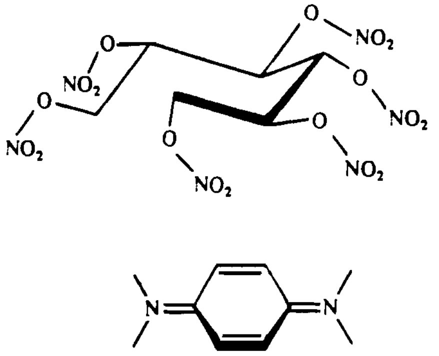


IV

The comparison of the enthalpy of the formation of Wurster cation of primary, secondary and tertiary butyl nitrate has shown that the primary ONO_2 group is the weakest electron acceptor and the strongest is the tertiary ONO_2 group the enthalpy of formation ($-\Delta H_f$) being 0.47 and 0.61 kcal/mol respectively. Nitroglycerine, pentaerythritol tri- and tetranitrates reacted with TMPD at the molar ratio 1:1. The same ratio was observed with erythritol tetranitrate but comparison with pentaerythritol tetranitrate (PETN) shows a stronger electron accepting property of the former probably due to the presence of secondary nitrate groups.

Hexanitrates of hexitols show strong accepting properties: 1 mole of hexanitrates with 2 moles of TMPD, in agreement with the rule – 3 ONO_2 groups for 1 mole of TMPD.

More detailed examination of the electronic spectra of TMPD with pentanitrates of D-xylitol, D-mannitol and hexanitrates of D-mannitol, D-sorbitol, D-dulcitol and myoinositol has shown three stages of the reaction in 1,2-dichloroethane as a solvent. At first all of them showed a rapid formation of low intensity transient bands between 909 and 1030 nm, which corresponds to an unstable CT–complex. Within 15 min (as in the case of all other nitrate esters) two bands of Wurster cation appeared. While these bands of nitrate esters persisted for a few days, both bands of pentanitrates and hexanitrates disappeared within 2 hours and were transformed into one band of 450 nm characterizing the yellow coloured relatively stable complex of the ratio 1:1 of hexanitrates to TMPD. The enthalpy of the formation of the new complex was $-\Delta H_f = 5.12$ kcal/mol, a value of the same magnitude as in many π–π complexes. Following the 'overlap and orientation principle' of Mulliken [18] the structure of the 1:1 complex was rationalized [15] being as shown on formula V. (Fig. 40, p. 308).



V

The structure of TMPD is represented here as TMPD being transformed into a quinoid compound: tetramethyl-*p*-quinonediamine dication formed by disproportions of Wurster cation. Its structure was confirmed by infra red spectroscopy.

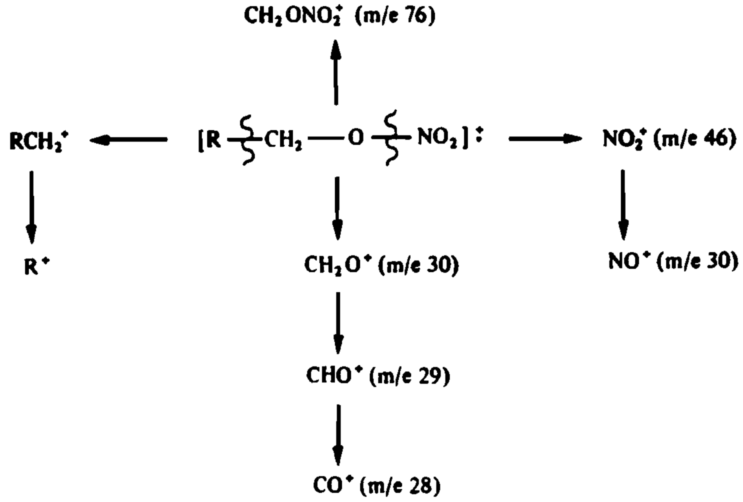
A hypothetical structure of complexes of nitrate esters with one to four nitrate groups was also advanced [19]. It was suggested that TMPD be used for analytical detection (including TLC) of nitrate esters [20].

In the light of the above work the finding of Parihar, Sharma and Varma [21] on the colour reaction of *O*-nitro compounds with potassium sulphanilate and α-naphthylamine in acetic acid should also be attributed to the oxidation of amines. The reaction produced the coloured cations and possibly charge–transfer complexes between the *O*-nitro compounds and the amine.

Further experiments were carried out on CT complexes between D-mannitol hexanitrate and pyrimidine and purine bases important in biochemical processes [22]. A summarized report has also been given on nitrate esters as electron acceptors [23].

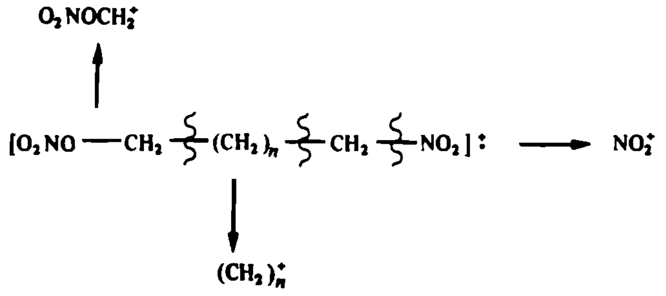
Fraser and Paul [159] examined nitrate esters by mass spectrometry. Both mononitrates and polynitrates were examined. The main conclusions of this important work are given below.

n-Alkyl mononitrates are subject to cleavage as:



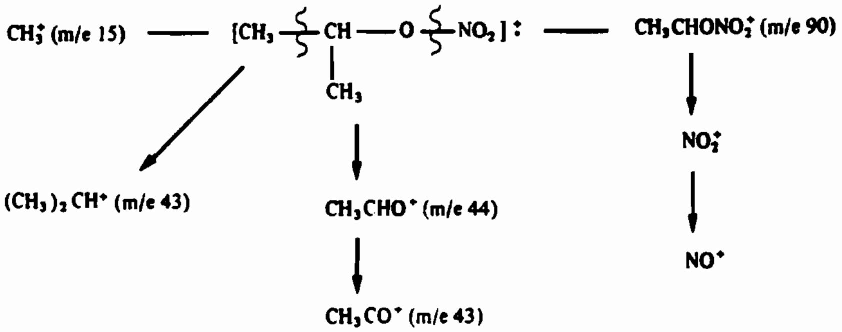
(1)

Diol dinitrates:



(2)

Branched-chain nitrates, for example isopropyl nitrate:



(3)

Nitroglycerine shows a low intensity peak of 76 m/e.

Kriemler and Buttrill [161] studied the formation of positive and negative ion-molecules from ethyl nitrate by ion cyclotron resonance technique. They found three kinds of reactions of positive ions:

(a) transfer of NO_2^+ from $CH_2ONO_2^+$ and $H_2NO_3^+$ to ethyl nitrate to form $C_2H_5N_2O_5^+$,
(b) protonation of $C_2H_5ONO_2$ by $C_2H_3^+$, $C_2H_5^+$ and CHO^+,
(c) fragmentation of protonated ethyl nitrate into $H_2NO_3^+$ and ethylene.

Negative ions have been found $C_2H_3O^-$, $C_2H_5^-$ and OH^- to produce NO_3^-.

HYDROLYSIS OF NITRATE ESTERS (Vol. II, p. 7)

Baker and co-workers (Vol. II, p. 8; [23–25]) have undertaken extensive research on alkaline hydrolysis of nitrate esters. Their results, as those of the other authors [27], were reviewed [2, 3]. They can be summarized as follows:

Nucleophilic attack on carbon (S_N1 and S_N2):

$$HO^- + RCH_2-O-NO_2 \longrightarrow RCH_2-OH + NO_3^-. \tag{4a}$$

Nucleophilic attack on nitrogen (S_N2):

$$HO^- + RCH_2-{}^{18}O-NO_2 \longrightarrow [R-CH_2-{}^{18}O + HONO_2] \longrightarrow RCH_2-O-H + NO_3^-. \tag{4b}$$

Nucleophilic attack on α-hydrogen (E2):

$$HO^- + RCH_2-O-NO_2 \longrightarrow RCH=O + NO_2^- + H_2O. \tag{4c}$$

Nucleophilic attack on β-hydrogen (E1 and E2):

$$HO^- + RCH_2CH_2-ONO_2 \longrightarrow RCH=CH_2 + NO_3^- + H_2O. \tag{4d}$$

Thus both cleavage of bonds C–O and O–N can occur.

The reaction of primary and secondary mononitrate esters are slow, for example slower than alkaline hydrolysis of carboxylic esters.

Primary nitrate esters can undergo alkaline hydrolysis mainly by two pathways (4a and 4b) and the yield of elimination reactions (4c and 4b) are, generally speaking, negligible.

Secondary nitrate esters give a more complicated picture. The dominating reaction is S_N2 but reactions (4c) and (4d) are of importance. Reaction (4c) can yield (depending on R) 8–45% of the carbonyl compound in addition to a certain amount of alkenes. A striking example was given by Baker and Easty [23] on hydrolysis of isopropyl nitrate (Vol. II, p. 13). An important contribution to the mechanism of the reaction of hydrolysis was given by Crystol and co-workers (Vol. II, p. 14) while reacting optically active 2-octyl nitrate.

Reaction (4c) E2 [24] has been used to introduce a carbonyl group into steroids [28].

Neutral hydrolysis of primary and secondary nitrates is very slow [23]. On the contrary, simple tertiary nitrate esters are readily hydrolysed [23, 27, Lucas and Hammett (Vol. II, p. 8)] to yield either alcohol (S_N1) or olefin (E1). Both go through the tertiary carbonium ion.

The four modes of hydrolysis can explain the reaction of nitrate esters with other nucleophiles such as ammonia and amines, hydrazine (Vol. II, p. 12), hydroxide and alkoxide ions (S_N1 and S_N2). Here the esters can act as alkylating agents.

Alkaline hydrolysis at 25°C of glycerol trinitrate, 1,2-glycerol and 1,3-glycerol dinitrates, 1-glyceryl and 2-glyceryl mononitrates with CO_2 free aqueous calcium hydroxide was studied by Capellos and co-workers [103]. They found that 2-glyceryl mononitrate isomerized on hydrolysis to 1-glyceryl mononitrate and 1,2-glycerol dinitrate isomerized to the 1,3-dinitrate before the hydrolysis was accomplished. 1,3-Glycerol dinitrate furnished on hydrolysis glicydyl nitrate in agreement with the reactions described in Vol. II, p. 128.

Nitrate ester hydrolysis is not catalysed by mineral acids to an appreciable extent [29, 26]. This is in contrast to nitrite esters which readily hydrolyse in an acid medium. According to Dewar [30] nitrate esters are protonated preferentially at the alkoxy oxygen according to equation (5a):

$$R\text{–}ONO_2 + H^+ \overset{\text{fast}}{\rightleftharpoons} R\text{–}O^+\text{–}NO_2 \xrightarrow{\text{slow}} ROH + NO_2^+ \tag{5a}$$

The last stage of the reaction is inhibited by the large positive heat of the dissociation [3].

In concentrated sulphuric acid nitrate esters are almost completely dissociated according to equation (5b):

$$RONO_2 + 3H_2SO_4 \longrightarrow ROSO_3H + NO_2^+ + H_3O^+ + 2HSO_4^-. \tag{5b}$$

Such a system can be used as a strong nitrating agent (Vol. I, pp. 15, 122). The nitration of an active methylene group with nitrate esters was basically described in Chapter I.

An interesting method of hydrolysis of nitrate esters to alcohols was given by Pews [158]. It consists in refluxing nitrate esters with formic acid followed by refluxing with methanol. Pentaerythritol trinitrate yielded pentaerythritol.

REDUCTION OF NITRATE ESTERS (Vol. II, p. 18)

The review on nitrate esters [2] should be mentioned here. The following are agents which can be used to recover the original alcohols: $LiAlH_4$, sulphides, H_2 on Pd/charcoal, Raney Ni, Pt. The reduction on platinum can go as far as to the formation of ammonia from ONO_2. Grignard reagent can be also used to reduce nitrate esters [31]. Reduction has been used to remove the *O*-nitro group which served for protection of OH during the synthesis of some steroids [32, 33].

Polarography can be used as an analytical method of quantitative determination of *O*-nitro groups. It was applied to simple esters [34] and to nitroglycerine [35].

CONVERSION OF NITRATE ESTERS INTO NITROALKANES

Bachman and Connon [37] described an interesting reaction of conversion of nitrate esters into nitroalkanes according to (6):

$$RONO_2 + NaNO_2 \xrightarrow{\text{solvent}} RNO_2 + ROH\ (\text{from RONO}) \qquad (6)$$

The reaction of nitrate esters with metal nitrites (e.g. sodium nitrite) was carried out in a suitable solvent at temperatures below 100°C. The nature of solvent is decisive to the yield. In the instance of *n*-propyl nitrate the best result (42% of 1-nitropropane) was obtained by keeping the reagents for one hour at 45°C in hexamethylphosphamide. The rest of the nitrate ester was converted to the original alcohol (54% of *n*-propyl alcohol in the described example).

The reaction has little value for the preparation of nitroalkanes, but is of theoretical importance as it indicates the reactivity of nitrate esters. It should be added that J. B. Levy [59] has found that thermal decomposition of nitrate esters resulted in the formation of small amounts of nitroalkanes. Thus the formation of nitroalkanes from nitrate esters seems to merit a more detailed examination of the mechanism of the conversion and decomposition.

FORMATION OF NITRATE ESTERS (Vol. II, p. 20)

The review by Van Dolah and co-workers [2] should be mentioned. Owing to the fact that sulphuric acid in a nitrating mixture promotes hydrolysis of nitrate esters, it is often desirable to nitrate alcohol with nitric acid alone in the presence of urea. The method was used on a large scale to make iso-propyl nitrate [36]. Urea obviously is a scavenger of nitric oxides and nitrous acid – compounds which can lead to oxidation and often dangerous decomposition.

Other nitrating agents which are the source of NO_2^+ ion can also be used (Chapter I).

An interesting method of making nitrate esters consists in reacting dinitrogen pentoxide with alcohols in a vapour phase as developed by Bachman and Connon [3, 37]. A continuously working laboratory nitrator was described by Connon [3]. Here N_2O_5 is produced as a dilute mixture with oxygen by reacting $NO_2(N_2O_4)$ with ozonized oxygen and has a composition according to the diagram (7):

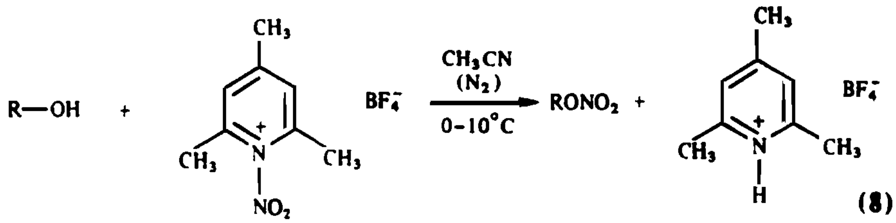
$$NO_2 + O_3 \rightleftharpoons NO_3 + O_2 \longrightarrow N_2O_5. \tag{7}$$

The addition of N_2O_4 to alkene oxide can also produce nitrate esters. E. White and Feldman [38] reacted with a solution of N_2O_4 on sodium butoxide–butanol at $-75°C$, and received butyl nitrate with a yield of 89%. The reaction is also an example of N_2O_4 acting according to equation (16), Chapter I, as ion pair nitronium nitrite ($NO_2^+ + NO_2^-$). The order of adding reagents is critical: the reversed nitrosation can occur due to the action of N_2O_4 in the capacity of nitrosyl nitrate ($NO^+ + NO_3^-$) – equation (17), Chapter 1. This was substantiated by Bachman and Connon [3, 37]. They also found that sodium hydroxide can be used instead of sodium butoxide.

A convenient laboratory method for the preparation of nitrate esters consists in acting with silver nitrate on alkyl bromide or iodide in nitromethane or nitrobenzene [2] or acetonitrile [3]. Kornblum and co-workers [39] made an extensive study of the stereochemistry and mechanism in the reaction of silver nitrate (and nitrite) with alkyl halides. Their conclusion can be summarized: the optically active nitrate esters (as well as nitrite esters) are produced with an inversion. Thus optically active 2-bromooctane when treated with silver nitrate gives 2-octyl nitrate of the inverted configuration regardless of the solvent. With α-phenylethyl chloride however, the steric course of the reaction is solvent dependent: in ethyl ether and in benzene α-phenylethyl, nitrate is produced with retention of configuration but in acetonitrile or petroleum ether the nitrate ester is produced with the inversion. The authors came to the conclusion that the reaction of silver salts with alkyl halides is rationalized as concerted S_N1–S_N2 processes.

Nitrate esters are formed as by-products in the reaction of alhyl bromide or iodide with silver nitrite [40]. By using a temperature below 0°C the formation of nitrate ester can be prevented [41].

Olah and co-workers [42] suggested a convenient and safe method for the preparation of alkyl nitrates (particularly polynitrates) via transfer nitration of alcohols (polyols) with *N*-nitrocollidinium tetrafluoroborate according to scheme (8)



(8)

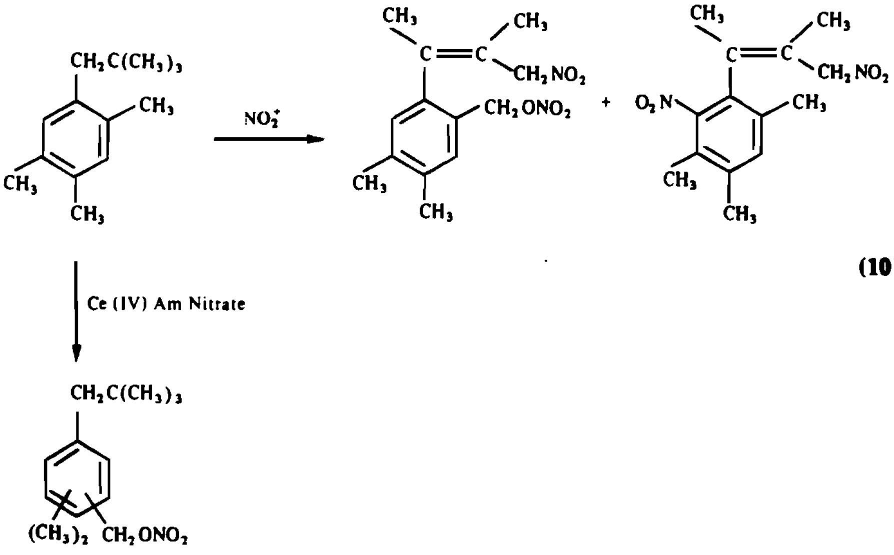
The yield is 41–100%, thus ethyl nitrate, glycol dinitrate and nitroglycerine can be obtained in theoretical yield.

Among the other methods of formation of nitrate esters the reaction discovered by Franchimont [43] of the action of nitric acid on nitramines is of importance:

$$CH_3NHNO_2 \xrightarrow{HNO_3} CH_3ONO_2 + N_2O. \qquad (9)$$

The reaction should be taken into consideration when examining the formation of nitramines including Cyclonite.

Interesting reactions of the formation of nitrate esters consist in the action of some nitrating agents on alkanes and alkyl groups. Titov and Shchitov [44] established that cyclohexane, *n*-heptane and *n*-octane react with dinitrogen pentoxide to yield cyclohexyl, 2-heptyl and 2-octyl nitrates respectively. Suzuki and co-workers [45] described the action of an excess of nitric acid or cerium ammonium nitrate on 2,4,5-trimethylneopentylbenzene and found that compounds were formed with one of the methyl groups subjected to nitro-oxidation according to abridged scheme (10)



(10)

In another series of experiments Suzuki and associates [46] found a similar reaction of nitration $CH_3 \longrightarrow CH_2ONO_2$ by acting with nitrous acid on pentamethyl derivatives of acetophenon.

Nitrate esters can also be made by the oxidation of nitrite esters (Vol. I, p.2). This reaction can also be carried out through a photolysis of nitrite esters. Such is, for example, the photolysis of octyl nitrite in heptane saturated with oxygen of the probable mechanism as below [47, 48]:

$$\begin{aligned} & C_8H_{17}ONO + h\nu \rightleftharpoons C_8H_{17}O\cdot + NO, && \text{(a)} \\ & 2NO + O_2 \rightleftharpoons 2\,NO_2, && \text{(b)} \quad \text{(11)} \\ & C_8H_{17}O\cdot + NO_2 \rightleftharpoons C_8H_{17}ONO_2. && \text{(c)} \end{aligned}$$

The yield was 50%.

Bachman and Connon [49] have shown that simple nitrite esters can be partly oxidized to corresponding nitrate esters by mixtures of N_2O_4 and oxygen which probably react as N_2O_5 or free radical NO_3. The same authors [37] obtained nitrate esters by reacting nitrite esters with a mixture of N_2O_4 with ozonized oxygen according to (7). Octyl nitrite gave a 70% yield of the nitrate as well as 30% octanoic acid. When octyl nitrite reacted with dilute ozonized N_2O_4 (which reacted as N_2O_5) in a counter current reactor [3] the yield of octyl nitrate could be as high as 97%.

GAS-CHROMATOGRAPHY OF ALKYL NITRATES

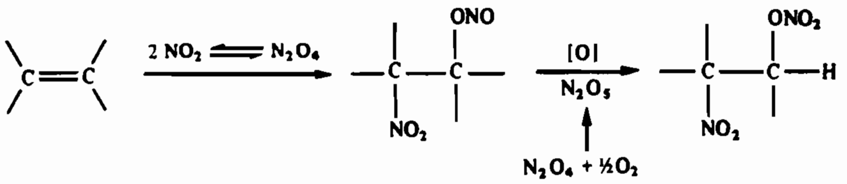
Although analytical problems are not discussed in the present book, it is appropriate that some information should be given, as the problem of the presence of nitrate esters, for example in air, is connected with problems of safety.

Alkyl nitrates can be separated and identified by gas–liquid–chromatography. Ethylene glycol succinate was used as the partition liquid and Celite C22ak was used as support [155]. Gas–liquid chromatography was used to determine nitrate esters in the presence of aromatic nitro compounds [156]. An improvement was made in the gas-chromatography by using an electron capture detector with tritium source [157].

ALKENES AS A SOURCE OF NITRATE ESTERS

As pointed out in Vol. I, p. 146 nitrate ester of β-nitroethanol can be formed by passing ethylene into a nitric–sulphuric acid mixture, and a side reaction is the formation of ethylene glycol dinitrate. However in most experiments nitronitrate ester is the minor product of the reaction. The reactions of alkenes with N_2O_4 were described in the excellent review paper by Shechter [50]. The classic work of N. Levy, Scaife *et al.* (Vol. I, pp. 594–5); [51–53] should be mentioned here, as well as those of Lachowicz and Kreuz [54], Bonetti and co-workers [55], Stevens [56].

Connon [3] summarized their results in two schemes. The simple version is (12).



(12)

Here the oxidizing agent can be N_2O_5 or $\cdot NO_3$ which can be formed by the action of oxygen on $NO + NO_2$ [57].

An interesting method for the formation of an iodo nitrate ester consists in acting with $Hg(NO_3)_2$ and iodine on alkene [58].

NITRATE ESTERS AS EXPLOSIVES (Vol. II, p. 2)

Relatively little work has been dedicated to the examination of such problems as the rate of detonation of nitrate esters, except in the instance of new compounds or those which are not yet sufficiently known. They are now reported in a description of the said compounds. On the contrary, considerable work has been done on thermal decomposition of nitrate esters. Particularly numerous are papers by Soviet authors mainly those of Andreev and his School collected in three monographs [60–62]. The data on the energy of activation of thermal decomposition of nitrate esters and the frequency factors are collected in Table 47 [63–65]. The calculated figures are remarkably similar for all nitrate esters and also are in agreement with those formerly found for nitroglycerine – Vol. II, p. 50. It should also be pointed out that the energy of activation is greatly influenced by the temperature of experiments – see [76, 77].

Determination of stability remains largely unchanged and is much the same as described in Vol. II, p. 23. The 'Heat test' (Abel test) is frequently used to determine the purity of nitrate esters such as nitroglycerine, glycol dinitrate, DGDN and nitrocellulose because of its simplicity [66].

Fraser [67] examined the stability of nitrate esters by determining the hydrolysis rates of the esters using sodium hydroxide in 90% ethanol at 30° and 60°C. The reactions are all second order in both nitrate ester and hydroxide ions. As the measure of the stability of an ester Fraser took the initial specific rate of hydrolysis. His results are summarized in Table 48.

He concluded that stability increases as the length of the carbon chain increases and is further enhanced by the introduction of an α-methyl group. Alkyl substitution in β-position has a smaller but similar effect. The replacement of a hydrogen by methyl or substituted methyl group decreases the rate of hydro-

TABLE 47. Energy of activation of nitrate esters

Compound	Energy of Activation kcal/mol	log B	Temperature ranges °C	References
Ethyl Nitrate	39.0	15.5	100–170	64b
Nitroglycerine	39.0	15.4	80–140	64c
Ethylene Glycol Dinitrate (Nitroglycol)	39.0	14.5	80–140	64c
Diethylene Glycol Dinitrate	42.0	16.5	80–140	64c
1,2-Propylene Glycol Dinitrate	40.3	15.8	72–140	65
1,3-Propylene Glycol Dinitrate	39.1	14.9	72–140	65
1,4-Butylene Glycol Dinitrate	39.0	15.1	72–140	65
2,3-Butylene Glycol Dinitrate	41.6	16.7	72–140	65
Mannitol Hexanitrate	38.0	15.9	80–140	64c
PETN	40.0	15.8	80–140	64c
Nitrocellulose (13.35% N)	39.2	15.0	100–170	63
Collodion Cotton	38.0	14.4	70–140	64a

TABLE 48. Initial second order rates of hydrolysis of nitrate esters [67]

Compounds	$10^5 k_1$	
	30°C	60°C
Methyl nitrate		112
Nitroethyl nitrate	1050	
n-propyl nitrate		2.9
n-butyl nitrate		2.9
iso-butyl nitrate		1.6
Ethylene glycol mono-nitrate	168	2700
Ethylene glycol dinitrate	160	
1,3-Propane diol dinitrate	58.7	1300
1,4-Butane diol dinitrate		16.0
DGDN		140
Triethyleneglycol dinitrate (TEGDN)		340
1,2-Propane diol nitrate	54	4650
1,3-Butane diol nitrate	20	
2,3-Butane diol nitrate	2.9	66
Metriol trinitrate (trimethylol-methylmethane trinitrate)	69	
Nitroglycerine	24000	
1,3-Glycerol dinitrate	4500	66200
1-Glycerolmononitrate	2150	51000
2-Glycerolmononitrate	920	20500
Nitro-iso-butyl glycerol trinitrate	128000	
PETN	34	2700

lysis (compare the rate of *n*-propyl and iso-butyl nitrates, nitroglycerine and metriol trinitrate).

The recent novel use of nitrate esters (in addition to their primary role as constituents of high explosives and propellants) is also directed towards improving the ignition and burning of liquid fuels, for example isopropyl nitrate (p. 306). Curme [68, 69] suggested the addition of polyethylene glycol nitrate and polypropylene nitrate as an addition to liquid fuel. Currently experiments are being carried out in Brasil on adding a small proportion (*ca.* 3%) of nitroglycerine to ethanol used as engine fuel (p. 299).

BIOLOGICAL ACTION OF NITRATE ESTERS

According to Von Oettingen [70] nitrate esters oxidize haemoglobin to methaemoglobin and, by depression of the muscles in the vascular walls, cause a peripheral vasodilatation resulting in lower systolic blood pressure, and increased pulse and respiratory rates. The maximum permitted concentration in working places differs for different nitrate esters: a typical example is nitroglycol with a maximum permitted concentration of 1.5 mg/m^3.

GLYCEROL TRINITRATE (NITROGLYCERINE (Vol. II, p. 84))

Setting Point

Some new data have appeared on the physical properties of nitroglycerine. Such is the determination of the setting point by Andreev and Bezpalov [71] on highly pure nitroglycerine. Nitroglycerine was purified by molecular distillation at 40–50°C under pressure of $10^{-4}-10^{-5}$ Torr. After two or three distillations the setting point +13.1 was found. The authors considered this method for the purification of nitroglycerine to be the most efficient and the safest.

However Meyer [72, 73] gives slightly higher setting points for nitroglycerine:

+13.2 [72] and +13.2–13.5 [73] for stable modification,
+ 2.2 [72] and + 1.9–2.2 [73] for labile modification.

Vapour Pressure (Vol. II, p. 43)

The data on vapour pressure of nitroglycerine were collected by Meyer [72, 73] as being:

0.00033 millibar at	20°C
0.0097	50
0.13	80
0.31	90

Absorption Spectra (Vol. II, p. 45)

The shoulder on the band of asymmetrical and symmetrical vibrations is due to the rotational isomerism [4–7]. Also it should be attributed to the fact that nitroglycerine contains both primary and secondary nitrate groups which according to T. Urbański and Witanowski [5] give different frequencies of asymmetric vibrations (p. 281).

Chemical Properties and Stability (Vol. II, pp. 46–47)

Thermal decomposition of nitroglycerine (and other similar nitrate esters) has been studied intensively by Soviet Union authors and their work has been described in collective volumes [61, 62] and the monograph by Andreev [60].

Here are the main conclusions of some of these important works as presented by Andreev and Bezpalov [71, 74]. They examined the action of water (at 80°, 100° and 120°C) and nitric acid (at 100°C).

Figure 37 shows the decomposition of nitroglycerine in the presence of 0.03% of either nitric acid or water or both, as compared with pure nitroglycerine. The decomposition was recorded by the pressure which developed inside the closed vessel. The strongest action was produced by nitric acid alone, less active was pure water and still less active nitric acid with water. The authors explain it in terms of different rates of hydrolysis and oxidation–reduction processes.

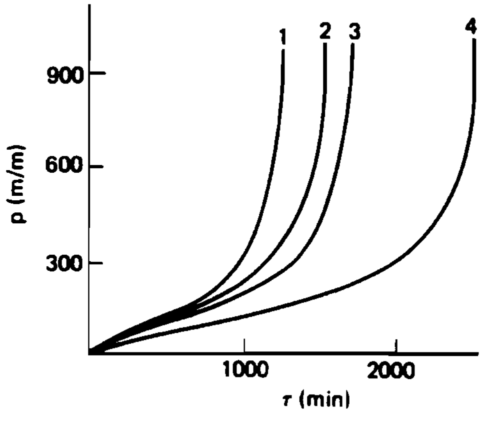


FIG. 37. Influence of a small quantity of water and nitric acid (0.3%) on decomposition of nitroglycerine at 100°C [74]. 1. NG + nitric acid. 2. NG + nitric acid + water. 3. NG + water (0.3%). 4. pure NG.

Larger quantities of nitric acid (0.13–1.5%) with water produce a characteristic shape for the curve of decomposition – Fig. 38. It comprises three stages:

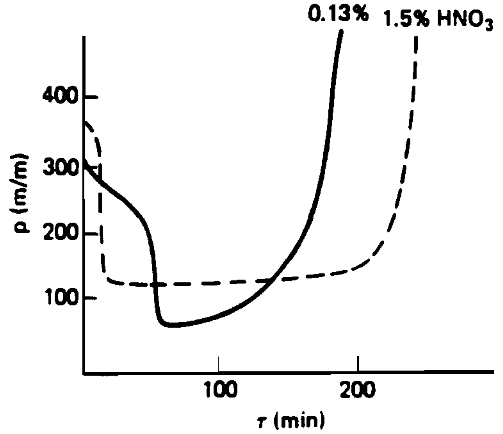


FIG. 38. Influence of nitric acid (0.13% and 1.5% HNO_3) on decomposition of nitroglycerine in the presence of water [74].

(a) induction period under constant pressure,

(b) rapid fall of pressure, due to the reactions between the products of hydrolysis,

(c) increased pressure due to decomposition and oxidation.

The practical conclusion drawn by the authors was that moist nitroglycerine may become dangerous in storage if it contains traces of acid, for example, from insufficient washing.

Svetlov [75] examined the thermal decomposition of pure nitroglycerine in the range of 80–140°C. Two stages have been found. The first is not influenced by the products of the reaction. This is followed by the second stage when the products of the decomposition greatly influence the rate of the reaction. This is presented in Fig. 39. The value of log $\Delta p/\Delta\tau$ is greatly influenced by δ-density inside the container of the sample.

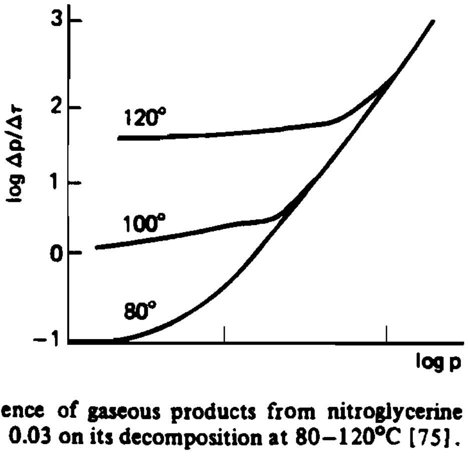


FIG. 39. Influence of gaseous products from nitroglycerine at density δ = 0.03 on its decomposition at 80–120°C [75].

Gorbunov and Svetlov [76] confirmed these findings for the temperature range 80–140°C. The energy of activation depends on the range of temperatures: at 80–140°C and 100–140°C it was found to be 28 kcal/mol and 32 kcal/mol. As previously pointed out (p. 293) the energy of activation is greatly influenced by the temperature range of experiments. Thus Wenograd [77] found value $E = 21.8$ kcal/mol for nitroglycerine at temperatures 300–1000°C.

Gorbunov and Svetlov [76] also examined the role of water in the decomposition of nitroglycerine. Thus water has a very strong influence particularly at higher temperatures, whereas nitric acid increases the rate of decomposition at lower temperatures. As a consequence Gorbunov [78] determined the solubility of water in nitroglycerine at 20–90°C. It varies from 0.26% at 20°C to 0.97% (weight %) at 120°C. The solubility increases when nitroglycerine contains some (0.3–0.6%) nitric acid.

As already reported, Fraser and Paul examined nitrate esters, among them nitroglycerine, by mass spectrography [159].

Recently Caire-Maurisier and Tranchant [160] examined thermal decomposition of nitroglycerine at 110°C using NMR, infra red and mass spectrometry and gas chromatography techniques. Mass spectrometry fragmentation suggested the formation of such fragments as: N_2^+, NO^+, NO_2^+, CO^+, CO_2^+, CH_2O^+, $CH_2ONO_2^+$, $CH_2{-}CHO^+$, $CHO{-}CH_2ONO_2^+$ and fragments with a nitrite ester group, for example $CHONO{-}CH_2NO{-}CH_2ONO^+$, $CHONO{-}CH_2ONO^+$.

Sensitivity to Impact

Bowden and Yoffe [79, 80] pointed out the role of small trapped gas bubbles in the sensitivity of both liquid and solid explosives. The adiabatic compression of small trapped gas bubbles creates 'hot spots' manifested by high temperature. Also friction occurs at the surface of the containing walls, on grit particles or between the crystals of explosives and forms an additional factor governing the sensitivity of explosives to impact.

This was confirmed by a number of authors, their work has been collected in monographs by Afanasyev and Bobolev [81] and Dubovik and Bobolev [82] and in the paper by Coley and Field [83]. The collapse of air bubbles is shown to lead to an increase of sensitivity of liquid explosives by:

(a) local increase of the deflagration velocity and
(b) generating a pressure pulse which is capable of producing hot spots.

This explains the data on the high sensitivity to impact of liquid nitroglycerine and relatively low sensitivity of solid nitroglycerine (Vol. II, p. 53).

The air bubbles produce a type of micro-Munroe jet oriented in the direction of the shock.

Burning of Nitroglycerine

Nitroglycerine burns readily in open vessels under atmospheric pressure. When confined it burns more readily under reduced pressure, for example 0.5 atm. When confined in a tube nitroglycerine burns under atmospheric pressure if the diameter is larger than 0.5 mm. The rate of burning at the critical diameter of 0.5 cm is 0.14 cm/sec. [60]. Andreev and Bezpalov [84] indicated that the critical diameter of burning of nitroglycerine under pressure within the range 20–100 atm is still reduced. They pointed out that three diameters exist:

d_1 – the smallest which allows normal burning,
d_2 – the largest which allows normal burning, beyond which extinguishing can occur due to turbulent phenomena and heat losses,
d_3 – the increase of that diameter gives normal burning.

Under atmospheric pressure the diameters d_1, d_2 and d_3 are 0.5, 2.6 and 7.5 mm respectively.

The increase of viscosity of nitroglycerine by dissolving nitrocellulose reduces the ability of nitroglycerine to burn under turbulent conditions and reduces the critical diameter. The same author gave critical diameters of:

Ethylene glycol dinitrate	1.0 mm
DGDN	5 mm

The ability of nitroglycerine to burn is now being utilized (on a large experimental scale) to improve the burning of ethanol being used as a fuel for car-engines in Brasil. A small proportion (*ca.* 3%) is added to ethanol for this purpose, so far with a positive result [108].

Explosion and Detonation of Nitroglycerine (Vol. II, p. 51)

Andreev [85] described his experiments on the thermal decomposition of nitroglycerine and the possible transformation into an explosion. The decomposition is speeded up by the reaction products. The rate of decomposition depends very much on the concentration of the products and much less on the temperature, in agreement with former findings of Roginskii (Vol. II, pp. 47–48).

Two different rates of detonation of nitroglycerine (explosion and detonation) (Vol. II, pp. 54–55) became the subject of experiments and discussions, for example, Taylor [86], Häuseler [87] and Soviet workers [88, 89]. It has also been shown that the reaction front in homogeneous liquid explosives becomes distorted under conditions close to failure [9, 91].

Coley and Field [83] discussed the LVD (low velocity detonation) in liquid explosives. According to the author of the present book the LVD should be called not the detonation, but the explosion (Vol. II, pp. 54–55). In order not to create confusion the term LVD will be accepted. Coley and Fields [83] pointed out that LVD in liquid explosives systems is a stable reaction regime, readily initiated by shock pressures of a few kilobars with propagation velocity of the order of 2000 m/s. The thermodynamic theory of detonation is not applicable to this regime since the pressures involved are too small for direct shock heating of homogeneous explosive to be significant. According to Coley and Fields new experiments have shown that the presence of gas or vapour filled cavities within the explosive is an essential requirement for initiation and propagation of LVD [91–95].

In liquid explosives bubble size becomes an important factor – this was pointed out by Coley and Field [84]: small bubbles facilitate the transfer to LVD.

Zimmer [96] came to the conclusion that the LVD of nitroglycerine (1500–1600 m/s) could be manifested by a spiral mode of propagation. (It should be pointed out that T. Urbański [97] expressed the view that non-homogeneous explosive mixtures can show a spiral way of detonation.) According to Zimmer the irregularities of the LVD are caused by the interaction of incident and reflection waves forming Mach waves under certain conditions. An analogy can be drawn between the spiral way of detonation of gas-mixtures [98–102] and spiral way of detonation of solid–liquid systems.

The critical diameter in a steel tube is 24 mm according to Meyer [72, 73].

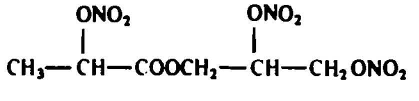
Specifications for glycerine and nitroglycerine are given in Chapter XI on the manufacture of nitroglycerine.

GLYCEROL DINITRATES ('DINITROGLYCERINE') AND DERIVATIVES

'Dinitroglycerine' is a common impurity present in nitroglycerine. Most frequently it is glycerol 1,3-dinitrate. 1,2-Isomer is usually present in negligible quantity. Krasiejko [104] isolated the dinitrates by TLC and spectrometrically determined the nitrites obtained by hydrolysis of dinitrate. (The chromatography of nitroglycerine has been described in a few papers prior to the work of Krasiejko [105–107].)

Glycerol dinitrate does not currently have a practical application.

Glycerol-nitrolactate Dinitrate (VI) [72, 73]

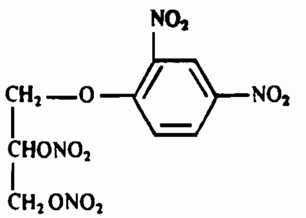


$$CH_3-\overset{ONO_2}{\overset{|}{C}H}-COOCH_2-\overset{ONO_2}{\overset{|}{C}H}-CH_2ONO_2$$

VI

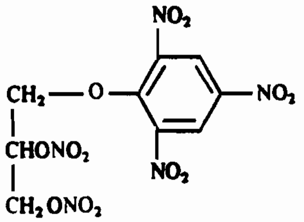
This is an oily substance of density 1.47 and ignition temperature 190°C obtained by the nitration of glycerol mono lactate. It is a good gelatinizer of nitrocellulose.

Glycerol 2,4-Dinitrophenylether (VII) and Trinitrophenylether (VIII) Dinitrates [72, 73]



VII

m.p. 124°C



VIII

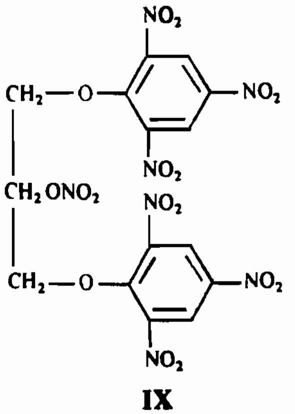
m.p. 128.5°C

Here are some pertinent data on the properties of the substances:

	VII	VIII
Ignition temperature	205–210°C	200–205°C
Lead block	320 cm^3	420 cm^3
Sensitivity to impact	0.8 kpm	0.4 kpm
Gelatinization of nitrocellulose	poor	none

Both compounds VII and VIII can be obtained by the nitration of *o*-nitrophenylglycerol ether and phenyl glycerol ether respectively.

Hexanitrodiphenylglycerol Mononitrate (IX) [72, 73]



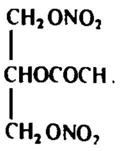
IX

m.p. 160–175°C

The wide range of melting temperatures indicates the decomposition of the substance during heating. The substance gives lead block test of 355 cm^3. It is much less sensitive to impact than VII and VIII due to the presence of only one *O*-nitro group. It was obtained by dissolving glyceryl diphenyl in nitric acid followed by mixing the solution with nitric–sulphuric acid.

Mixed Esters of Glycerol

Among esters of glycerol with nitric and organic acids the most important appears to be Glycerol Acetate Dinitrate (X) described by Meyer [72, 73]



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CHOCOCH_3 \\ | \\ CH_2ONO_2 \end{array}$$

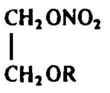
X

This is an oily substance of density 1.42 with ignition temperature 170–180°C. It gives lead block test 200 cm^3. It was prepared by nitration of acetylglycerol with mixed acid rich with nitric acid.

GLYCOL NITRATES

Ethylene Glycol Mononitrate (2-Nitratoethanol) (Vol. II, p. 142)

Glycol mononitrate has aroused a certain amount of interest. Twist and Baughan [109] examined the vapour pressure of the solution of this substance, and of a number of other nitrate esters, and found the deviations from Raoult laws to be of the same order as those observed by Chédin and Vandoni for nitrocellulose [110]. Prior to this work Marans and Zelinski [111] prepared a number of mixed esters of the type XI where R are unsaturated acyls apt to polymerize and thus to give combustible polymers.

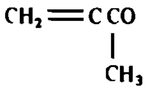


$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2OR \end{array}$$

XI

R is $CH_2{=}CHCO$

(a)



$$\begin{array}{l} CH_2{=}CCO \\ \quad\;\; | \\ \quad\; CH_3 \end{array}$$

(b)

$CH_3CH{=}CHCO$

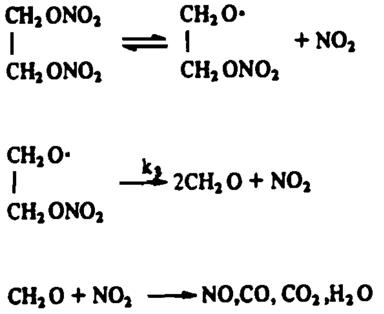
(c)

They acted on 2-nitratoethanol with chlorides of acrylic (a), methacrylic (b) and crotonic (c) acids in the presence of cuprous chloride as a polymerization inhibitor. The radical polymerization was initiated by benzoyl peroxide in nitrogen atmosphere. It lasted 20 min at 100°C. In the absence of a catalyst polymerization occurred at 20°C in the course of a few days. This observation is in agreement with the finding reported in Vol. II, p. 19 that nitrate esters can catalyse polymerization reaction, contrary to *C*-nitro compounds (Chapter IV).

Ethylene Glycol Dinitrate ('Nitroglycol') (Vol. II, p. 142)

Relatively less attention is now paid to ethylene glycol dinitrate. It is currently used in mixture with nitroglycerine for low freezing dynamites but some mining explosives, used in countries with harsh winters, contain nitroglycol alone.

Kondrikov [112] rationalized thermal decomposition of ethylene glycol dinitrate by diagram (13):



$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \rightleftharpoons \begin{array}{l} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{array} + NO_2 \qquad (a)$$

$$\begin{array}{l} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{array} \xrightarrow{k_1} 2CH_2O + NO_2 \qquad (b) \quad (13)$$

$$CH_2O + NO_2 \longrightarrow NO, CO, CO_2, H_2O \qquad (c)$$

Ethylene glycol dinitrate is more toxic than nitroglycerine because of its higher volatility. According to Meyer [72, 73] the maximum permitted concentration in a work place is 1.5–1.6 mg/m^3.

Diethylene Glycol Dinitrate (Vol. II, p. 149)

Diethylene glycol dinitrate – DGDN has currently become the most important (next to nitroglycerine and nitroglycol) *O*-nitro compound, much in use in 'double base' propellants. The great advantage of DGDN is its relatively low sensitivity to impact and subsequently safer handling than nitroglycerine and good solubility of nitrocellulose. The disadvantage is in the danger produced by spent acid (Vol. II, pp. 152–153).

Svetlov [113] examined thermal decomposition of DGDN in the liquid phase in the temperature range 60–150°C. He calculated the energy of activation – see Table 47 (p. 294).

Lurge and Svetlov [114] examined the decomposition of DGDN in the presence of oxygen, NO_2 and NO, H NO_3 and oxalic acid at 80–120°C and found that nitric and oxalic acids can increase the rate of decomposition up to one hundred times. Oxygen also increases the rate of decomposition but to a much smaller extent. The first stage of the reaction consists in binding oxygen, probably due to the formation of peroxides. The latter decompose at a later stage.

The specification for diethylene glycol for nitration is given in Chapter XI.

Triethylene Glycol Dinitrate (Vol. II, p. 154)

This substance was used (together with diethylene glycol dinitrate) in Germany during World War II for making double base propellants. It is less volatile than diglycol dinitrate but more soluble in spent acid (Vol. II, p. 155).

The specification for triethylene glycol for nitration is given in Chapter XI.

Butine-2-diol-1,4 Dinitrate

$$O_2NOCH_2C\equiv CCH_2ONO_2$$

XII

This substance was obtained by T. Urbański and Tarantowicz [115]. The aim was to produce an explosive of a greater power considering that the acetylenic bond increases exothermic properties of the substance. In lead block it gave a better performance (385 cm^3) than tetryl and ethylene glycol mononitrate.

It is an oily substance of density (at 20°C) 1.408. On a hot plate, temperature 245–380°C, it gave a violent explosion similar to that of nitroglycerine. Below 245°C it evaporated and above 380°C took on a spheroidal shape and burned quietly. It is more sensitive to impact than nitroglycerine, and is a good solvent for nitrocellulose.

The substance gives a negative heat test (Abel test): at 80°C potassium iodide-starch paper was coloured after 3 min.

The diol dinitrate (XII) was obtained in a standard way by nitrating in the acid mixture composed of 40% nitric and 60% sulphuric acid at 18–22°C. The yield was 70–75% of the theoretical.

NITRATE ESTERS OF MONOHYDROXYLIC ALCOHOLS
(Vol. II, p. 160)

The main interest in nitrate esters of monohydroxylic alcohols lies in their application as rocket fuels. Subsequently a thermal decomposition of nitrate esters is examined. Kondrikov [112] gave the following diagram (14) of the thermal decomposition of nitrate esters of a general formula RCH_2ONO_2:

$$\left.\begin{array}{lr}
RCH_2ONO_2 \longrightarrow RCH_2O + NO_2 & (a)\\
RCH_2O \longrightarrow R\cdot + CH_2O & (b)\\
CH_2O + NO_2 \longrightarrow NO, CO, CO_2, H_2O & (c)\\
RCH_2O + NO \longrightarrow RCH_2ONO & (d)\\
RCH_2O + NO \longrightarrow RCHO + NOH & (e)\\
2NOH \longrightarrow N_2O + H_2O & (f)
\end{array}\right\} \quad (14)$$

A few other schemes of thermal decomposition are given with the description of particular nitrate esters.

All the mono-nitrate esters give a colour reaction with tetramethyl-*p*-phenylene-diamine due to Wurster cation [13–15, 22a]. The colour remains for several days.

With regard to the nitration of alcohols attention should be drawn to the work of Eremenko [140] who pointed out the role of undissociated nitric acid in the *O*-nitration mechanism.

Methyl Nitrate (Vol. II, p. 160)

Some properties of methyl nitrate, such as the thermal decomposition and explosive properties are given in Vol. II. Some additional data are given by Meyer [72, 73]:

boiling point	65°C
density	1.217
heat of explosion	1462 kcal/kg
volume of gases	873 l/kg
critical diameter in a steel tube	18 mm

Methyl nitrate was found to be present in the products of the decomposition of azomethane ($CH_3{-}N{=}N{-}CH_3$) when the latter substance was subjected to ultraviolet irradiation [116]. This was due to an intermediate formation of CH_3O_2 radical which reacted with NO to yield the nitrate ester:

$$CH_3O_2^{\cdot} + NO \longrightarrow CH_3O\cdot + NO_2 \longrightarrow CH_3ONO_2. \tag{15}$$

Ethyl Nitrate ($C_2H_5ONO_2$) (Vol. II, p. 163)

Ethyl nitrate is currently an important component of liquid rocket fuel. In that respect considerable work is being done to elucidate the mechanism of thermal decomposition by Pollard, H. S. Marshall and Pedler [151]. Some fragments of their mechanism are as follows (16):

$$\begin{aligned} &C_2H_5ONO_2 \longrightarrow C_2H_5O\cdot + NO_2 \\ &C_2H_5O\cdot \longrightarrow CH_3CHO + H \\ &C_2H_5O\cdot \longrightarrow HCHO + CH_3^{\cdot}, \text{etc.} \end{aligned} \tag{16}$$

Considering the formation of a number of simple molecules and free radicals, such as $CH_3^{\cdot}$, $CH_3O\cdot$, NO, NO_2, CO, CO_2 several less defined reactions can take place, for example, the formation of nitrite esters [2]:

$$\begin{aligned} &C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO, \\ &CH_3^{\cdot} + O \longrightarrow CH_3O\cdot, \\ &CH_3O\cdot + NO \longrightarrow CH_3ONO, \text{etc.} \end{aligned} \tag{17}$$

Nitrite esters are marked by their relatively low stability (p. 318).
Meyer [72, 73] gives some additional data on the properties of ethyl nitrate:

melting point	−102°C

heat of explosion	913 kcal/kg
volume of gases	1227 l/kg
lead block test	420 cm^3

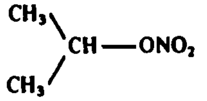
For the activation energy see Table 47.

The preparation of ethyl nitrate follows the same rule as that of methyl nitrate: nitric acid should be free of nitrous fumes by adding urea (Vol. I, p. 162).

n-Propyl Nitrate (Vol. II, p. 165)

n-Propyl nitrate has found an application as a liquid fuel in rockets according to Meyer [72, 73]. The same source gives data on the properties of the substance.

Iso-Propyl Nitrate (Vol. II, p. 165)



$$(CH_3)_2CH{-}ONO_2$$

XIII

As previously pointed out a practical application has been found for iso-propyl nitrate. It was originally believed [117] that the substance could only be made from iso-propyl iodide and silver nitrate. Direct nitration was found to yield mainly acetone due to the oxidation of the secondary alcoholic group. However a process of continuous nitration of iso-propyl alcohol in the presence of urea has been described by Imperial Chemical Industries patents [36]. iso-Propyl alcohol and urea were introduced into nitric acid (over 40% HNO_3) at its boiling temperature and a current of air stirred and removed unstable products. According to Desseigne [118] the method gave *ca.* 80% yield. He used nitric acid of over 50% HNO_3 at 108–110°C.

iso-Propyl nitrate is in use as an engine starter fuel [119] and for rockets [121].

Gray and co-workers [120] examined the decomposition of iso-propyl nitrate at elevated temperatures:

$$\text{i-}C_3H_7ONO_2 \longrightarrow 1.5\,CO + 0.5\,CO_2 + CH_4 + H_2 + 0.5\,H_2O + 0.5\,N_2 \qquad \textbf{(18a)}$$

with the thermal effect $-\Delta H = ca.$ 86 kcal/mol. Gray *et al.* [121] also examined the decomposition of iso-propyl nitrate at elevated temperatures (290–1380°C). In the absence of oxygen the reaction can be depicted by equations:

$$\begin{aligned} &\text{i-}C_3H_7ONO \longrightarrow \text{i-}C_3H_7O\cdot + NO_2 \\ &\text{i-}C_3H_7O\cdot \longrightarrow CH_3^{\cdot} + CH_3CHO \qquad \textbf{(18b)} \\ &CH_3^{\cdot} + NO_2 \longrightarrow CH_3NO_2. \end{aligned}$$

Acetaldehyde, nitrogen dioxide and nitromethane are main products of the decomposition. In the presence of oxygen methyl radicals yield formaldehyde. Acetaldehyde is very reactive and by abstraction of hydrogen yields acetyl which is the principal source of CO and CO_2:

$$\begin{aligned} &CH_3CO \longrightarrow CH_3^{\bullet} + CO \\ &CH_3CO + NO_2 \longrightarrow CH_3^{\bullet} + CO_2 + NO. \end{aligned} \tag{19}$$

POLYHYDROXYLIC ALCOHOL ESTERS (Vol. II, p. 166)

Butane-1,2,4-triol Trinitrate (Vol. II, p. 166)

Meyer [72, 73] gave some data on the properties of the substance, such as:

freezing point	−27°C
density	1.52
oxygen balance	−16.6%
heat of explosion	1420–1470 kcal/kg.

1,2,4-Butanetriol is nitrated to trinitrate with a nitric–sulphuric acid mixture. The nitrated product shows good stability. It is less volatile than nitroglycerine and according to Meyer is in use for tropic-proof double base powder.

Erythritol Tetranitrate, Erythrol Tetranitrate (Vol. II, p. 100)

Meyer [72, 73] gives some data:

melting point	61.5°C
deflagation point	154–160°C with a violent explosion
density	1.6
heat of explosion	1443 kcal/kg
volume of gases	704 l/kg.

It has an intense magenta colour with tetramethyl-*p*-phenylene-diamine due to Wurster cation [13–17].

Pentitol Pentanitrates (Vol. II, p. 168)

D-Xylitol pentanitrate with tetramethyl-*p*-phenylene-diamine (TMPD) gives a blue colour due to the formation of Wurster cation after which another charge–transfer complex is formed by 2 moles of xylitol pentanitrate and 1 mole of TMPD dication formed from Wurster cation [13–17].

D-*Mannitol Pentanitrate* (Vol. II, p. 170)

D-Mannitol-1,2,3,5,6-pentanitrate (m.p. 81–82°C) is prepared by heating hexanitrate of mannitol with pyridine [120]. Denitration occurs with the evolution of nitrogen dioxide. D-Mannitol pentanitrate reacts with TMPD in much the same way as D-Xylitol pentanitrate forming a charge–transfer complex of 2 moles of mannitol pentanitrate and 1 mole of the dication [15].

D-*Mannitol Hexanitrate* (Vol. II, p. 168)

According to Elias and Hayward [123] the nitration of D-mannitol to hexanitrate can be carried out with N_2O_5 vapour at 0 ± 2°C under reduced pressure. After two hours the hexanitrate was formed with 100% yield.

The charge–transfer between D-mannitol hexanitrate and TMPD is best presented on Fig. 40 according to T. Urbański *et al.* [15]. Curve I shows a CT colourless complex at *ca.* 1030 nm which disappears after 5 min, and two maxima of Wurster cation (570 and 620 nm) appear. The intensity of the latter increased in the course of 15 minutes (curve II).

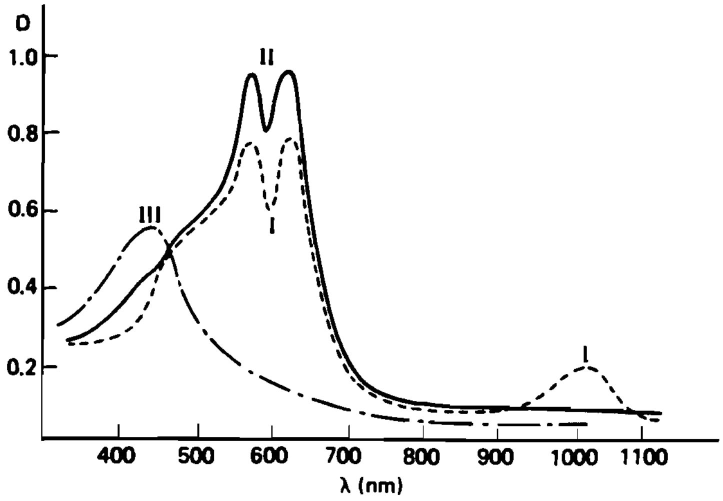
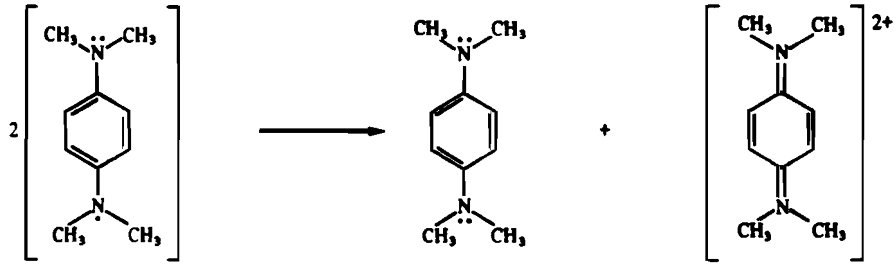


FIG. 40. General shape of electronic spectra of hexanitrate of D-mannitol and tetramethyl-*p*-phenylenediamine charge transfer phenomenon.

After 2 hours both maxima vanished and a new maximum at 450 nm appeared (curve III). The yellow coloured complex is formed from 1 mole of mannitol hexanitrate and 1 mole of TMPD dication. The dication is formed as the result of the disproportionation between the Wurster cation and TMPD:



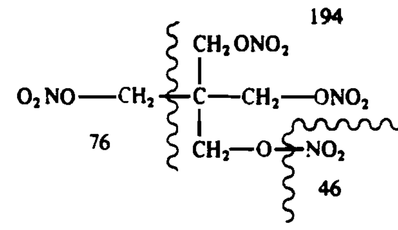
(20)

The stereochemistry of the complex is rationalized by diagram V (p. 285).

It was suggested that a six-member chain of mannitol hexanitrate was coiled into a pseudo-ring. It is not surprising if one considers that long chain organic substances in solution have a tendency to be coiled. This is based on thermodynamical analysis, dipole measurements etc. [124].

Lurye and Svetlov [125] examined the thermal decomposition of mannitol hexanitrate in the temperature range 80–140°C. They came to the conclusion that the decomposition of molten hexanitrate occurred in two (at least) stages. The first stage is manifested by splitting off nitrogen dioxide. This stage follows the equation of Arrhenius (Table 47). After that secondary reactions occur – mainly of oxidation accompanied by hydrolysis with formed water.

Mass spectrometry showed the decomposition occurs according to XIV [159]



XIV

Meyer [72, 73] gives some data on the explosive properties of D-mannitol hexanitrate:

heat of detonation	1420 kcal/kg
volume of gases	694 l/kg
deflagration point	185°C

*Dulcitol (*D*- or -*L*-galactitol) Hexanitrate and* D*-Sorbitol hexanitrate*

(Vol. II, pp. 171, 172)

Both substances can be obtained with 85 and 94% yield respectively by nitrating dulcitol and D-sorbitol with N_2O_5 vapours under reduced pressure at 0 ± 2°C [123].

Both substances form charge–transfer complexes with tetramethyl-*p*-phenylenediamine in much the same way as D-mannitol hexanitrate [14, 15, 22a].

PENTAERYTHRITOL TETRANITRATE (PETN) (Vol. II, p. 175)

Some new data on the properties of PETN have been reported by Meyer [72, 73]:

melting enthalpy	36.4 kcal/kg
specific heat	0.26 kcal/kg
density	1.76

An important practical problem is how to obtain PETN in a crystalline shape which would allow an easy flow to a high bulk density, that is, greater than 1.1–1.2 g/cm³. The needle habit gives the lowest bulk density which can be used for certain purposes.

A fairly wide range of particle sizes can be obtained by adding water to an acetone solution of PETN and a bulk density of 1.1–1.2 can be reached. It is known that various sizes of crystals make the better filling of a container possible and can give a higher density.

Duncan [126] described experiments on crystal size and shape of PETN by its recrystallization.

To produce the substance having a high specific surface area $S_0 = 10$ to 20×10^3 cm²/g suitable for detonators a 'shock crystallization' was used. Pure PETN was dissolved in acetone (1:5) and the solution dropped into aqueous ethanol at *ca.* −30°C. The resulting crystals are much different in sizes (0.5–16 μ) and irregular shapes from spheres to needles. A modification of the method can be used by introducing a 10% solution of pure PETN in acetone–ethanol into ethanol–acetone (1:2) cooled to −20°C.

Crystallization from DMSO produces crystals which are too large. On the contrary, crystallization by spraying saturated acetone solution into an air tunnel gives very fine spherical particles when the tunnel walls are struck.

Duncan also gives a new table of the solubility of PETN in some solvents (Table 49).

The size of crystals increases by keeping them at 90–120°C for several hours (e.g. 20–30 hours).

Chromatography (TLC) showed very small spots of hexanitrate of dipentaerythritol (DPEHN), and in some cases octonitrate of tripentaerythritol (TPEON) and pentaerythritol trinitrate.

T. Urbański [127] suggested recrystallization to add a protective colloid such as an acetone solution of nitrocellulose (low viscosity grade collodium cotton).

TABLE 49. Solubility of PETN in wt.% according to Duncan [12b]

Solvent	Temperature °C						
	0	20	25	30	40	50	60
Methanol		0.46			1.15		2.60
Chloroform		0.09					
Carbon tetrachloride		0.096		0.108	0.118	0.121	
1,2-Dichloroethane		1.5		4.1	11.2		14.2
1,1,2,2-Tetrachloroethane		0.18		0.27	0.40	0.58	
2-Methyl-1-propanol	0.07	0.195			0.415		1.205
Nitromethane	3.34		8.89				
Ethyl acetate		13.0		17.0	22.0	31.0	
β-Ethoxyethyl acetate		1.5		4.1	7.6	11.2	14.2

PETN was examined by mass-spectroscopy [128]: electron impact gave two fragments: 76 and 46.

Field ionization fragments: 194, 76, 74 are depicted by scheme XIV.

Thermodynamic Properties and Thermal Decomposition of PETN

Dinegar and Stammler [129] determined enthalpies connected with the volatility of PETN. The enthalpies of sublimation and of vapourization were:

35 ± 3 kcal/mol and
19 ± 2 kcal/mol respectively.

A considerable number of papers have been dedicated to the thermal decomposition of PETN. They were reviewed by Andreev [71]. He quoted the work of Robertson [130] who examined the decomposition of PETN in the temperature range: 161–233°C, the energy of activation was

$$E = 47 \text{ kcal/mol}, \quad \log B = 19.8.$$

For a 5% solution of PETN in dicyclohexylphthalate at 171–238°C the values of E and B were:

$$E = 39.5 \text{ kcal/mol}, \quad \log B = 16.1.$$

Robertson analysed gaseous products while keeping PETN for 2 min at 210°C. He found (in mol %): 0.51 NO_2, 2.11 NO, 0.42 N_2O, 0.07 N_2, 0.09 H_2, 0.93 CO, 0.28 CO_2 and formaldehyde and water.

He suggests that the first stage of the decomposition of PETN consists in splitting off NO_2, after which $-CH_2O$ is removed as formaldehyde.

A different approach to the thermal decomposition of PETN was given by T. Urbański [131–133]. The shape of the curve of the induction time against the temperature is given in Fig. 41, much the same as in Vol. I, Fig. 13, p. 50 for nitroglycerine.

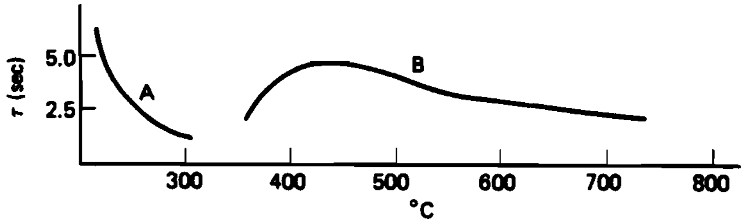


FIG. 41. Behaviour of PETN at high temperatures according to T. Urbański [131–133]. Induction period τ is given against the temperature. Curve B corresponds to spheroidal shape of the molten substance.

Curve A is of the usual shape induction period/temperature below 350°C. Curve B gives the induction period when the molten substance takes spheroidal shape. The activation energy was found to be:

E = 22.4 kcal/mol for the temperatures 240–310°C
E = 4.5 kcal/mol for the temperatures 460–790°C.

Wenograd [77] in the temperature range 400–1000°C established the energy of activation as E = 20.4 kcal/mol. Evidently the energy decreases with the increase of temperature.

Andreev and Kaidymov [134] published a review on the thermal decomposition of PETN and a description of their own results. Their data for activation energy are given in Table 47. They confirmed the results of T. Urbański and co-workers (Vol. II, pp. 181–183) and similarly of Tonegutti [135] and Bourjol [136] that the addition of aromatic nitro compounds to PETN lowers the stability of the latter. In all experiments it was shown that decomposition in the liquid phase, that is, the molten system, engenders faster decomposition than that of the solid phase.

According to the author of the present book lowering of the stability has the result that on melting the substance passes to a higher energy level with an increased entropy.

Differential Scanning Calorimeter (DSC) was used by Rogers and Dinegar [165] in combination with X-ray and microscopy to find the reason for anomalous behaviour in the heat of fusion of PETN crystallized by different methods. Microscopy revealed the existence of at least three crystal habits of PETN: (1) 'tetragonal', (2) needle, (3) irregular plates. Their heats of fusion ΔH_t were:

(1) 36.5–37.4 cal/g
(2) 36.5–37.7 cal/g
(3) 31.7–33.2 cal/g

Differences in heat of fusion was attributed to the lattice energy changes resulting from random inclusions within the lattice.

Explosive Properties

An interesting finding was made by Institut Franco-Allemand de Recherches de St. Louis [166] that the rate of detonation of PETN takes different values along different crystal axis:

(001)	8424 m/s
(110)	8887 m/s.

T. Urbański and Galas [137, 138] examined the rate of detonation of PETN with various liquids. The results with two liquids which do not dissolve PETN: water and glycerol are given in Table 50. The general trend of the change of the observed rate of detonation with the addition of a liquid is given in Fig. 42.

TABLE 50. Detonation of PETN with water and glycerol [137–138] in tubes 20/26 mm diameter, detonator No. 8 with 10 g PETN

Proportion of liquid	Density		Rate of detonation m/s		Difference V_O-V_r
	Total	Real ρ_r	observed V_O	at density ρ_r V_r	
Water					
0	1.45	1.45	7275	7275	0
5	1.45	1.38	7250	7055	195
10	1.45	1.31	7445	6810	635
20	1.45	1.16	7130	6250	930
30	1.44	1.01	6645	5530	1115
Glycerol					
5	1.40	1.33	7350	6880	425
10	1.40	1.26	7355	6080	1745
30	1.45	1.02	7675	5620	3055
35	1.45	0.94	7280	5230	2050

The observed rate of detonation of the explosive with the liquid was V_O and the total density 1.45. By adding a liquid and keeping the same total density (density of the mixture) the real density of the explosive was lowered to ρ_r which at this density gives the rate of detonation V_r. Hence V_O-V_r is the increase in the rate of detonation by adding the liquid. This is fully discussed in Chapter XIII (Table 60).

Dinegar, Rochester, Horton and Johnson [145] examined the shock sensitivity of PETN and came to the conclusion that the nature of the gas in a small scale 'gap-test' influences the sensitivity of PETN. Thus He, Ar, N_2 and CO_2 have a desensitizing effect, whereas oxygen sensitized the compressed charges.

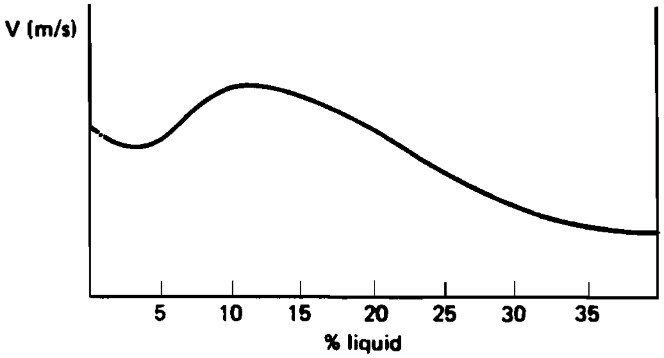


FIG. 42. Rate of detonation of systems: high explosive – non-explosive liquid, e.g. PETN or RDX and water or glycerin.

Nitration of Pentaerythritol (Vol. II, p. 185)

It is known that the nitration of pentaerythritol on an industrial scale is carried out mostly with nitric acid alone, without sulphuric acid. Therefore, it was necessary to establish the solubility of PETN in nitric acid of different concentrations and at different temperatures. Such data were given by Camera and Mauro [139] and are collected in Table 51. The same authors established the solubility of dipentaerythritol hexanitrate (Vol. II, p. 195) – Table 52.

TABLE 51. Solubility of PETN in nitric acid [139] in g of the substance in 100 g of the solution

% HNO_3	Temperature °C					
	0	10	20	30	40	50
60	0.018	0.041	0.109	0.352	0.645	0.880
65	0.036	0.113	0.322	0.778	1.020	1.300
70	0.075	0.134	0.302	0.845	1.570	2.240
75	0.069	0.124	0.265	0.557	1.340	2.650
80	0.106	0.195	0.335	0.650	1.291	2.775
85	0.190	0.329	0.585	1.056	1.957	3.849
90	0.441	0.762	1.318	2.314	4.036	7.156
95	1.060	1.825	3.023	4.822	8.090	12.609

Nevertheless, some industrial methods are still using mixtures of nitric and sulphuric acids and an important paper by Eremenko [140] has been published in which he gives an analysis of the role of nitric acid in nitric–sulphuric acid mixtures as applied to the *O*-nitration of alcohols in general and of pentaerythritol in particular. He gave a critical review of the work of Ingold and co-workers [141, 142] and their suggested mechanism of *O*-nitration based on reactions:

TABLE 52. Solubility of DiPEHN in nitric acid [139] in g of the substance in 100 g of the solution

% HNO_3	Temperature °C 0	10	20
60	0.024	0.064	0.222
65	0.080	0.246	1.099
70	0.271	0.530	1.455
75	0.526	0.926	2.309
80	1.358	2.693	5.798
85	4.674	7.911	18.23
90	18.26	26.17	38.02
95	30.51	46.43	54.64

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad \text{(a)}$$

$$NO_2^+ + ROH \rightleftharpoons ROH{\cdot}NO_2^+ \qquad \text{(b)} \quad (21)$$

$$ROH{\cdot}NO_2^+ + NO_3^- \longrightarrow RONO_2 + HNO_3. \qquad \text{(c)}$$

Eremenko questioned this trend of the reactions particularly in view of the facts described in Chapter I that nitric acid still possessed the nitrating ability at a concentration where the presence of NO_2^+ ions are excluded. With regards to *O*-nitration this was described by T. Urbański and Hackel [143]. By nitrating pentaerythritol and some ^{18}O labelled alcohols, Eremenko came to the conclusion that molecular, undissociated electrolytically nitric acid can be an agent for *O*-nitrating alcohols. He depicted this in diagram – Fig. 43 (in weight per cents) referred to *O*-nitration of pentaerythritol.

A summary of his conclusions, based on the analysis of the curves, is given here: region I limits the composition of the nitrating mixtures which transform

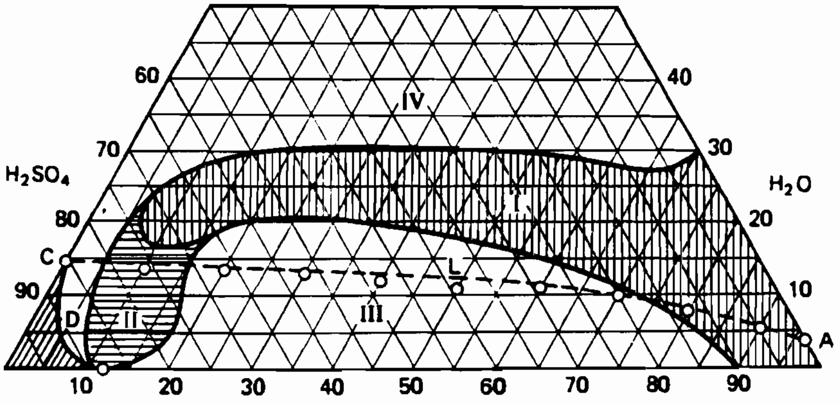
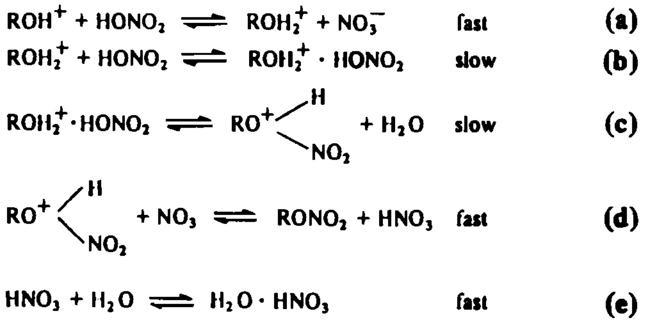


FIG. 43. Regions of the formation of pentaerythritol tetranitrate by nitrating mixture [144].

pentaerythritol into PETN with 94–98% yield without the formation of esters of sulphuric acid as intermediates. In region II the formation of PETN goes through the acid sulphates. In III tetranitrate is formed only in 10–50% yield with side reaction of oxidation accompanied by violent evolution of nitrogen oxides. In region IV *O*-nitration does not occur.

ALC curve shows the limit of the detection of NO_2^+ ions and the small region limited by curve CD shows the complete dissociation of nitric acid into NO_2^+ [144] and Vol. I, Fig. 9, p. 25 (in mol %). One can see that 'pure' *O*-nitration can occur in region I which is beyond the detectable NO_2^+ concentration.

Eventually Eremenko suggested the scheme of *O*-nitration (22):



$$\begin{array}{llll}
ROH^+ + HONO_2 \rightleftharpoons ROH_2^+ + NO_3^- & \text{fast} & (a) & \\
ROH_2^+ + HONO_2 \rightleftharpoons ROH_2^+ \cdot HONO_2 & \text{slow} & (b) & \\
ROH_2^+ \cdot HONO_2 \rightleftharpoons RO^+{<}^{H}_{NO_2} + H_2O & \text{slow} & (c) & (22) \\
RO^+{<}^{H}_{NO_2} + NO_3 \rightleftharpoons RONO_2 + HNO_3 & \text{fast} & (d) & \\
HNO_3 + H_2O \rightleftharpoons H_2O \cdot HNO_3 & \text{fast} & (e) &
\end{array}$$

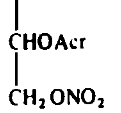
Proof of the accuracy of the scheme is also in the observed fact that the oxygen of nitrated alcohol remains in the nitrate. This was substantiated by nitrating alcohols labelled with ^{18}O.

MIXED PENTAERYTHRITOL AND GLYCEROL ESTERS (Vol. II, p. 191)

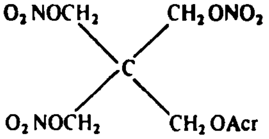
Recently a number of papers and patents have appeared which describe mixed esters of pentaerythritol and glycerol. Particular attention has been paid to esters containing one group of an unsaturated acid such as acrylic or methacrylic acid to produce an ester which could polymerize. The obvious aim is (in addition to that previously mentioned: Vol. II, p. 191): to produce combustible synthetic polymers, capable of being used as rocket propellants.

Mixed ethylene glycol esters have already been described (XI).

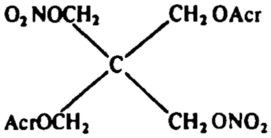
Wassmann [146] obtained mixed esters of glycerol and pentaerythritol as follows (Acr = acryl, methacryl):



XV



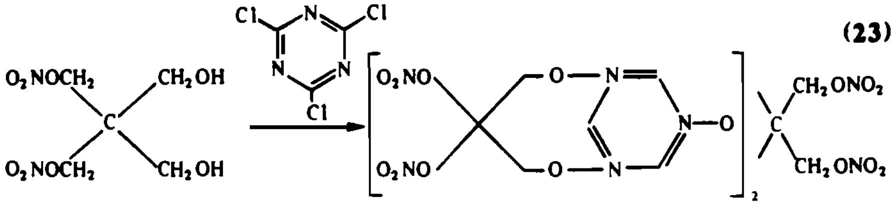
XVI



XVII

That will be mentioned in Chapter XXII dedicated to solid rocket propellants.

An interesting reaction of pentaerythritol dinitrate (PEDN) was reported by Matuszko and Chang [147]. It consists in reacting PEDN with cyanure chloride:



(23)

The reaction can serve as an analytical method of detecting PEDN.

METHOD OF PREPARATION OF PETriN and PEDN
(according to [148] and [149])

Pentaerythritol (80 g) was dissolved at 5°C in a *ca.* 6 times larger quantity of sulphuric acid (67%). CH_2Cl_2 (*ca.* 50 parts) was added followed by the addition of the nitrating mixture composed of sulphuric acid (98%) (72 g) and nitric acid (96%) (232 g) at 5°C. After mixing for 75 min, water (1000 cm^3) was added. The organic phase was neutralized with 10% $NaHCO_3$, evaporated to dryness and the solid was extracted with ether to eliminate PETN which was not dissolved.

The solution was cooled to −60°C to eliminate the precipitated impurity. On evaporation the trinitrate – PETriN (40 g) resulted. It contained some PETN and PEDN and was purified while removing PEDN by dissolving it in water.

The part insoluble in water was crystallized from CH_2Cl_2. Finally pure PETriN was obtained by distillation under reduced pressure. Under 1 mmHg a fraction of 155–160°C was collected. Precaution should be taken: it can explode at 175°C. It has m.p. 27–28°C (Vol. II, p. 194).

The aqueous solution was evaporated to dryness and furnished PEDN.

Camera [149] draws attention to the fact that PETN in spent acid is readily subjected to hydrolysis leading to the formation of tri- and dinitrate of pentaerythritol at different temperatures (20 and 40°C) and concentration of nitric acid (70–90%).

He calculated the constants of equilibria:

$$\frac{[\text{PE-TRi N}]\ [\text{HNO}_3]}{[\text{PETN}]\ [\text{H}_2\text{O}]} = K_1$$

$$\frac{[\text{PE-Di N}]\ [\text{HNO}_3]}{[\text{PE-Tri N}]\ [\text{H}_2\text{O}]} = K_2$$

The values of K_1 and K_2 are given in Table 53.

TABLE 53

Concentration %HNO_3	K_1		K_2	
	20°C	40°C	20°C	40°C
70%	0.996	1.362	0.608	0.726
80%	0.873	1.395	0.606	0.721
90%	0.950	1.396	0.749	0.838

The solubility of PETriN and PEDN in nitric acid of different concentrations is given in Table 54.

TABLE 54. Solubility of tri and dinitrates of pentaerythritol according to Camera [149]

Concentration %HNO_3	Temperature °C			
	20°		40°	
	PETri N	PEDN	PETri N	PEDN
60	0.032	0.040	0.179	0.265
65	0.099	0.102	0.309	0.370
70	0.094	0.079	0.511	0.486
75	0.085	0.054	0.456	0.337
80	0.103	0.049	0.441	0.245
85	0.160	0.054	0.629	0.246
90	0.283	0.060	1.081	0.267
95	0.376	0.038	1.344	0.157

NITRITE ESTERS (O-NITROSO COMPOUNDS)

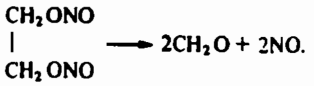
Nitrite esters (O-nitroso compounds) are usually not discussed as explosives. They are relatively unstable compounds but may possess some significance as products of the decomposition of *O*-nitro compounds according to Gray [150] and Pollard *et al.* [151].

Chemical and physico-chemical properties of O-nitroso compounds have been extensively studied by Steacie since 1934 [152] and described in a monograph [153].

An important work on the chemical stability and decomposition of ethylene dinitrite and glycerol trinitrite was done by Kondrikov [154]. Their activation energies were found to be:

at 170–190°C, E = 35.6 kcal/mol, log B = 13.8
and at 143–160°C, E = 41.6 kcal/mol, log B = 17.8 respectively.

The decompositions of the former can be depicted by diagram:



$$\begin{matrix} CH_2ONO \\ | \\ CH_2ONO \end{matrix} \longrightarrow 2CH_2O + 2NO. \qquad (24)$$

ESTERS OF OXY-ACIDS OF CHLORINE (Vol. II, p. 447)

Esters of oxy-acids of chlorine have not received any practical application owing to their very high sensitivity to impact and friction, but they are interesting from a theoretical point of view.

A few papers have appeared on the use of alkyl perchlorates, especially methyl perchlorate as alkylating (particularly methylating) agents [162]. Kevill *et al.* [163] established that methyl perchlorate in acetonitrile is a much weaker methylating agent than for example trifluoromethanesulphonate.

Geminal Diperchlorates

Baum [164] obtained geminal diperchlorates by reacting carbonyl compounds with perchloric acid in halogenated hydrocarbons: for example acetone and perchloric acid in chloroform yielded an oily product within a few minutes. This was 2,2-diperchloratopropane $(CH_3)_2C\ (OClO_3)_2$. It can be distilled: b.p. 52°C/0.1 mmHg.

It is very hygroscopic. Differential thermal analysis shows one exotherm peak at 159°C and second at 202°C which ended in an explosion at 250°C.

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APPENDIX

N-OXIDES (N→O)

An attention was recently drawn to explosive properties of N-oxides: N-hydroxyimidazole N-oxide (m.p. 183°) and its N-methoxy derivative [1]. The earlier finding [2] also reported that a care should be taken when purifying N-oxides by distillation. Thus low molecular weight N-oxides should be considered as possessing explosive properties.

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CHAPTER 11

PRODUCTION OF NITRATE ESTERS

(Vol. II, pp. 62–125, 185)

NITROGLYCERINE (NG)

No fundamental progress on methods of the manufacture of NG can be recorded. The main efforts have been concentrated on the problem of increasing the safety of the processes by using perfect automation with remote control devices, avoiding immediate contact between personnel and dangerous parts of the process and the reduction of the quantity of explosive in the working place. All these requirements can be achieved with continuous methods, although batch processes are still in use.

Continuous and semi-continuous methods are as described in Vol. II:

(1) Schmid (p. 99),
(2) Schmid-Meissner (p. 104),
(3) Raczyński (p. 106),
(4) Biazzi (p. 107),
(5) N.A.B. Injector Process (A.B. Gyttorp) (p. 114),
(6) Semi-continuous method of Jarek (p. 120).

Of the above methods 1, 2, 4 and 5 have been widely used in many countries. A novel method (7) has been described and is known as:

(7) Hercules Tubular Nitrator described by McKinney [1] and in *Encyclopedia of Explosives* [2].

Hercules Tubular Process

This description is based on that given in the Encyclopedia [2]. A continuous stream of glycerine flows through a tubular path to a tubular reaction zone where it meets a stream of precooled nitrating acid. The tubular reaction zone is uncooled, the temperature is controlled by regulating the temperature of precooled nitric acid and also the proportion of nitratic acid to glycerine. It is desirable to cool the mixture of nitrate ester and spent acid to facilitate the separation of the nitrated product.

The diagram of the system is presented in Fig. 44. Nitrating acid passes through pump 1 to the cooler, and valves 2 to 6 and meets glycerine in the

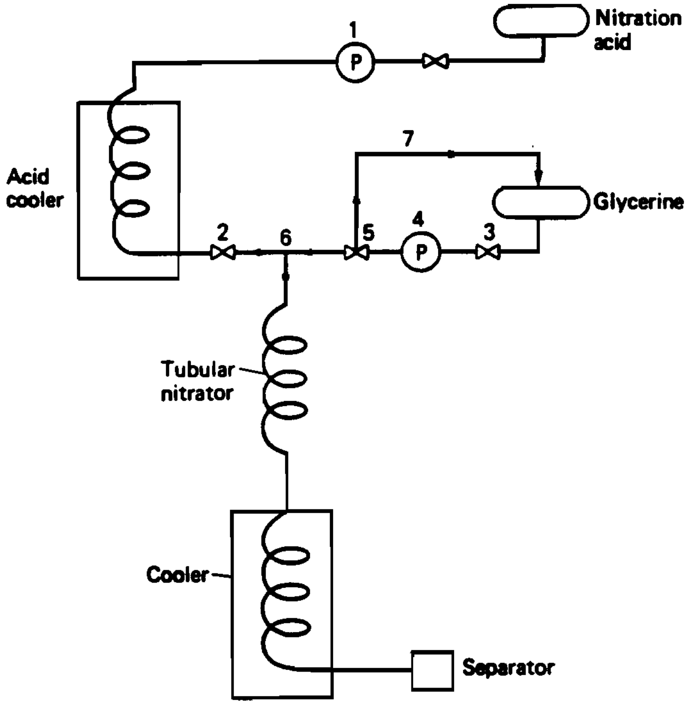

FIG. 44. Hercules Co. tubular nitrator of glycerine [2].

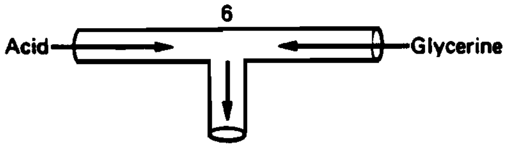

FIG. 45. T – tube for nitration of glycerine (Hercules Co.) [2].

counter current which enters through valve 3, pump 4 and valve 5 to the same place 6.

Nitration starts in 6 and continues in the tubular nitrator before entering the cooler and finally the separator. Valve 5 is a quick opening by-pass valve. In the case of an emergency valve 5 is turned to stop the flow of glycerine to the nitrator 6 switching through 7 to the glycerine container.

Figure 45 shows a diagram of the 'mixing tee' 6.

The nitrating acid in the Hercules Tubular Process is composed of 18–40% HNO_3, 45–70% H_2SO_4 and 11–17% H_2O. The preferred acid to glycerine ratio is 10–12 parts of acid per one part of glycerine.

Stow [3] improved the method by introducing a centrifugal separator of nitroglycerine from the spent acid.

The method can be used to both: nitration of glycerine, glycerine–ethylene glycerol mixture, diethyleneglycol or ethylene glycol.

Biazzi Process (Vol. II, p. 107)

The detailed description of the process given in Vol. II remains valid with a few additions described by Biasutti [4]. Figures 48 and 49 (Vol. II, pp. 108, 111) are still valid, and the main points which introduce some additional, novel information are given here.

Mixed acid and glycerine are stored externally in separate tanks and are transferred by means of centrifugal and gear pumps to small feed tanks. From the feed tanks the reactants are sent to the nitrator by means of two positive displacement pumps driven by the same electric motor. Two speed variators allow change in the total flow rate as well as the ratio between acid and glycerine. The glycerine feed pipe in the nitrator, fitted with a multi-nozzle distributing head is

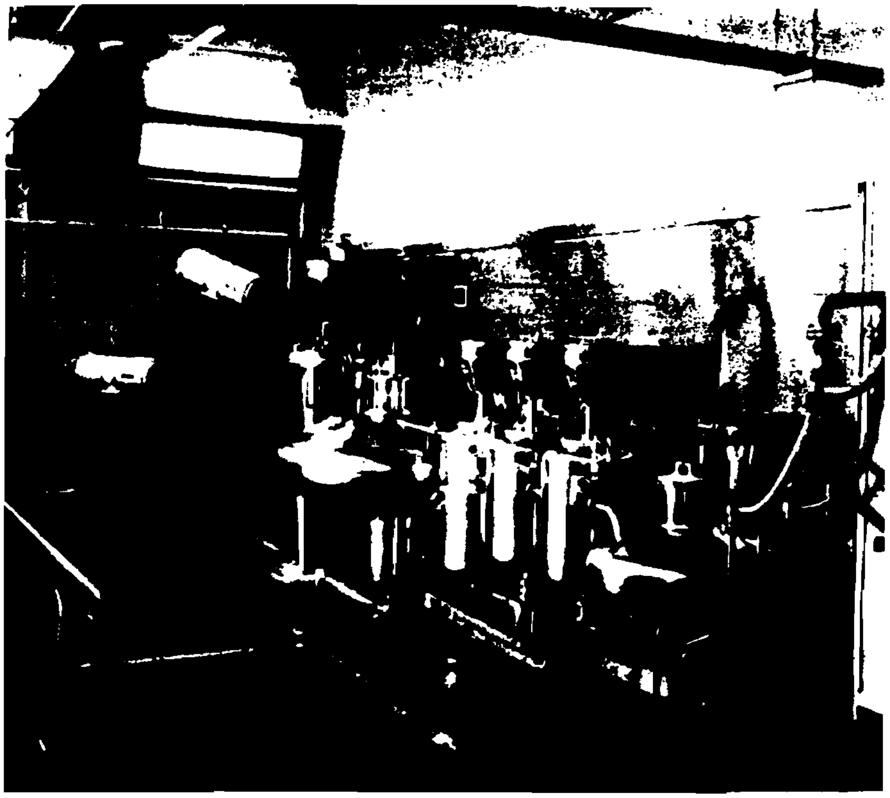

FIG. 46. Nitration of glycerine plant of M. Biazzi S.A. (Courtesy M. Biazzi S.A.).

retractable and can only be extended if all safety conditions are fulfilled. The feed arrangements are such that the acid and glycerine are quickly submerged, emulsified and forced down the nitrator through the central space formed by the cooling coils. Part of the emulsion overflows into the separator and part returns to the vortex in the nitrator fluid. Cooling is achieved by sodium nitrate brine circulating through helical coils. The reaction temperature is kept constant by thermostatic control of the brine valve.

The intensity of mixing in the nitrator by the turbine is such that the emulsion of nitroglycerine in the acid cannot be initiated by a No. 8 blasting cap. The turbine is driven by V-belts of a motor mounted in a room separated from the nitration unit by a partition wall.

The bottom of the nitrator is provided with a quick opening flap valve placed considerably off the axis which can be operated manually or pneumatically for quick draining of the contents into a large tank full of water.

Control of the Nitration

The emulsion overflowing from the nitrator enters the separator through a short section of pipe in which a special electrode is fitted for the measurement of the Redox-potential of the spent acid against a reference sample of mixed acid. The Redox-potential of the spent acid has a direct relation to the HNO_3 and HNO_2 content in this acid composed of $HNO_3-HNO_2-H_2O$ and can serve as a control on the extent that nitration follows the normal course without too many oxidation reactions and deviations from the normal course. It was first introduced by Öhman in 1938 [5]. He applied the method for the control of the nitration of glycerine [6–8], glycol and similar compounds [9] and eventually to the nitration of aromatic hydrocarbons [10]. More recently the method was extended by Camera [11] to the control of the nitration of pentaerythritol. See also a general description by Biasutti [12].

The Redox-potential of the system (1)

$$HNO_3 + 2H^+ \longrightarrow HNO_2 + H_2O \tag{1}$$

can be expressed by equation (at 20°C):

$$e = e_0 + 0.0291 \log \frac{[HNO_3]\ [H^+]^2}{[HNO_2]\ [H_2O]}, \tag{2}$$

where e_0 is the potential of the standard electrode. Considering that HNO_2 is relatively small and HNO_3 is constant at 20°C a simplified equation (3) can be used [13]:

$$e\ O\ e_0 = 0.0291 \log [HNO_2]. \tag{3}$$

The reference sample [11] is composed of

H_2SO_4	49.1%

HNO_3	48.3%
HNO_2	0.3%
H_2O	2.3%.

Nitrous acid is introduced into this solution in the form of $NaNO_2$.

By recording the value of e in mV the operator can see whether the trend of the reaction is normal. If the value of e deviates too much from normal, the nitration should be stopped by cutting the inflow of glycerine and, if necessary, the inflow of the mixed acid.

The following are some values of e in −mV given by Camera [11]:

TABLE 55. Values of e in mV

%HNO_3	%HNO_2			
	0.01	0.1	0.5	0.8
90	164	192	208	222
80	282	306	325	332
70	366	394	410	417

The permissible values of e should be established by experiments.

Separation of NG from the Spent Acid

From the tangential separator NG flows to the washing vessels and then to a storage tank. The spent acid flows from the base of the separator to its storage tank through a variable overlow valve by means of which the height of the nitroglycerine–spent acid interface may be controlled. This adjustment is effected automatically through a float on the spent acid layer in the separator. A small amount of water is added to the overflowing spent acid to avoid further separation of NG as in the system of Nathan *et al.* (Vol. II, p. 95).

Alkaline Washing of NG

Sodium carbonate solution is introduced to the first washing vessel by gravity. The automatic feed control is obtained by means of a pH-meter with its electrode placed at the outlet of the first washer. The soda water/NG emulsion passes through two additional washers for completion of the neutralization reaction. From the last washer the emulsion flows to a Biazzi separator. The wash water flows to a catch tank for the recovery of the last portions of unseparated NG.

Technical Data of Biazzi Method (Vol. II, p. 114)

Nitrator	
Heat Transfer Coefficient	700 kcal/m^2.h. °C

Ratio Coil Volume to Useful Volume	80/100
Ratio Coil surface to Useful Volume	10 m^2/100 l
Ratio Useful Volume to Production Capacity	110 l/1000 kg/h NG
Ratio NG content to Production Capacity	70 kg/1000 kg/h NG
Throughput of Emulsion through Turbine Wheel	10 m^3/min
Average Retention Time	4 min
Draining Time	8 sec
Separator	
Ratio total Volume to Production Capacity	800 l/1000 kg/h NG
Ratio Separated NG to Production Capacity	40 kg/1000 kg/h NG
Ratio total NG to Production Capacity	170 kg/1000 kg/h NG
Average Retention Time (NG)	10 min
Average Retention Time (Spent Acid)	50 min
Draining Time	20 sec
Washers	
Ratio NG/Production Capacity	50 kg/1000 kg/h NG
Retention Time (NG)	3 min

Safety Measures

When the Biazzi unit has to be shut down, it is necessary to remove all the NG from the nitrator–separator system. This is done by introducing spent acid from an overhead storage tank into the bottom of the nitrator until all the NG has been displaced through the overflow of the separator. A level sensor automatically stops the displacement process as soon as all the NG leaves the separator.

In general layout and design the possibility of the retention of a minute quantity of NG is eliminated. All the vessels are highly polished internally to prevent the adherence of NG to rough surfaces.

There are two control rooms. One is near the nitrator house in a 'control bunker', another is further away in a remote control room at a safe distance. The latter is provided with instruments to start, supervise Redox, pH NG–water emulsion and a device to shut down the unit. Both control rooms are provided with TV sets. Signals between the two houses are both electric and pneumatic, although controls on the nitration unit are only pneumatic. The remote control room is operated in case of emergency and necessity or breakdown of the automatic system.

The 'control bunker' is provided with a number of 'push buttons'. They are:

Preparation button. By pressing this button the nitrator and separator are filled with water, the pumps are started, brine is circulated through the cooling coils etc. When all red lights on the alarm panel are out the unit is ready to start.

The start button is then pressed, the glycerine pipe is extended to the nitrator, glycerine and mixed acids begin to flow at the selected production rate between the nominal rate (100%) and reduced to 50%.

The stop button causes the glycerine and acid flow to end and the glycerine pipe is retracted. One minute later the automatic shut-down sequence starts and continues until all the nitroglycerine has been evacuated from the building.

An alarm sounds in the case of irregularities.

The early history of the Biazzi invention was given by Biasutti [12].

Injector Nitration Process (Vol. II, p. 114)

Brunnberg [14] gave a brief description of the method and its early history.

Because of the high temperature of glycerine or glycerine–glycol mixture the viscosity is considerably reduced and helps the action of the injector. The temperature rise through nitration is 46–48°C. The influx of the alcohol is automatically regulated and registered. Only one second after the two components are mixed, cooling of the emulsion begins, first in a coil with cold water or brine and then in a tubular cooler with brine to reduce the temperature to +15°C.

The nitrate ester is separated in a centrifuge of 4–8 kg capacity. The spent acid contains 0.1% emulsified NG and by adding 4–5% water the nitroglycerine remains in the solution (Vol. II, p. 95).

The acid NG from the centrifuge runs to an injector where it is mixed with 8% aqueous solution of sodium carbonate. It is transported to a special degassing vessel, where CO_2 is evolved. After that the emulsion passes to two wash columns provided with perforated discs made of stainless steel. Mixing is achieved by air inlet to the column, from the second column the emulsion runs to a specially designed wash centrifuge. The stabilized nitrate ester runs to an injector and is transported as a non-explosive aqueous emulsion to a separate storage building.

From the point of view of safety, the main advantage of the injector method is the very small quantity of nitrate ester present in the reaction space and the very short reaction time (*ca.* 1 second). After the reaction has ended, the quantity of nitrate ester is too small to be able to detonate. If nitration is stopped, the emulsion flows downward, leaving the apparatus empty, cleaned by nitrating acid and subsequently there is no need for a safety tank for draining nitrate ester and acid in the case of emergency.

If the power fails or the reaction temperature becomes too high, a valve for the inlet of air to the injector opens automatically and prevents the alcohol being sucked into the injector. If the electric current returns, the nitration process cannot restart by itself.

Centrifugal separation of NG is safe on condition that lubrication is carried out according to instructions.

The injection nitration is supervised by remote control.

Safety Problems (Vol. II, p. 122)

Safety problems have already been tackled in the general description of processes. Biasutti [15] described over 20 accidents in nitroglycerine manufacture.

In the batch process two accidents were caused by faulty mixing. Thus in Gransberg, Sweden in 1955, the supply of compressed air to stir the content of the nitrator was stopped. Glycerine started to decompose which produced a heat evolution and hot acid together with decomposing organic substances entered the separator and detonated the charge of nitroglycerine in the separator (probably over 1000 kg).

Also in continuous methods of nitration faulty functioning of mixing in the nitrator has caused a few accidents. Another cause of accidents in continuous methods was the malfunctioning of the automation device which produced an inflow of the wrong proportions of glycerine and acid. Thus two accidents with the Schmid method (in Gyttorp, 1933 and in Bofors, 1953) and one with the Biazzi system (Kaohsiung, Taiwan, 1966) were caused by an insufficient proportion of acid in the unit. Insufficiently trained personnel can also be responsible for accidents where the production is fully automatic and requires skilled workers (e.g. wrong calibration and incorrect setting of control instruments).

A process for drying nitroglycerine with calcium chloride was probably the cause of an explosion of stored nitroglycerine in Schlebusch (1956). It is believed that drying with calcium chloride evolved enough heat to produce the decomposition of the substance.

Generally speaking storage of nitroglycerine should be avoided. The continuous methods were originally ended by batch processes of weighing and mixing nitroglycerine. By fully continuous methods no storage would be required. According to Biasutti [12] in Japan and Sweden for the manufacture of commercial explosives of *ca.* 500 kg/hr, only 40 kg of NG and 20 kg of dynamite can be present at any time.

A separate danger of handling nitroglycerine has recently been described. It consists in choe combined with adiabatic compression of minute air bubbles. The first described accident of this kind took place at Asa in Japan (1962). Meticulous study revealed that in the suction tube the air bubbles were originally under 0.1 atm, later the pressure increased to 1 atm. which caused a rise in the temperature by 300°C. A similar accident took place with a 'water hammer' it suddenly opening a water pipe which produced an adiabatic compression of air

(Marions, Illinois, 1968). A few more accidents produced by compressing air bubbles have also been reported [15].

Biasutti [16a] reported statistics of accidents which [16b] are given in Table 56.

TABLE 56. Accident statistics in ng manufacture

Number of accidents	Section
31	Nitration–Separation
66	Washing and Storage
13	After-Separation and Handling of Spent Acid
4	Wash Water Handling
2	Decontamination
15	Transportation

Accidents in the nitration–separation section were mostly due to self-decomposition of the NG–spent acid mixture following incorrect nitration ratio (9 cases), insufficient stirring (4 cases), leakage of cooling brine in the nitrator (2 cases), self-decomposition because of impure raw materials, instability of spent acid used for displacement. A high number of accidents during the washing and storage of NG have occurred mainly in older batch processes where the two sections were installed in the same building.

A great number of accidents have been caused by human error, for example the opening or closing valves on NG (9 cases), stumbling when carrying buckets full of NG (4 cases) shock of metal pieces (6 cases). Chemical decomposition was the cause of the explosion of nitroglycerine sludge accumulated at the bottom of settling tanks. External causes – lightning – caused 7 accidents. Spent acid decomposition was the source of 10 accidents. Here 5 cases were due to the decomposition of NG dissolved in the acid. Accidents in transportation were caused by stumbling, fall of buckets, shocks and derailments or collisions on mechanical transportation (6 cases). Transportation through water-injection was the cause of 8 accidents. This was due to adiabatic compression of air bubbles. Since the introduction of the safe water-injection method, where rapid energetic changes are avoided, the transportation by water-injection became much safer.

DIETHYLENE GLYCOL DINITRATE (DGDN) (Vol. II, p. 149)

As previously mentioned this compound was extensively used in World War II for making double base powder. It was made by the nitration of diethyleneglycol by methods similar to those used for the nitration of glycerine, preferably at higher temperatures (Vol. II, p. 151).

The specificiation of diethylene glycol for nitration was given by Meyer [17]:

Clear colourless liquid, density (20/4) 1.1157–1.1165
neutral to litmus
boiling analysis: five drops not below 241°C,
distillation at 246.5°C,
end not above 250°C
moisture: no more than 0.5%
residue after burning: no more than 0.02%
acidity (as H_2SO_4): no more than 0.01%
chlorides: traces
saponification number: not above 0.02%
reducing substances (test with ammonia solution of $AgNO_3$): none
viscosity at 20°C: 35.7 cP
Content of monoethyleneglycol – no more than 2%.

TRIETHYLENE GLYCOL DINITRATE (Vol. II, p. 154)

As already pointed out, the substance was used in double-base propellants in Germany during World War II.

Meyer [17] gives the specification of the glycol used for nitration (compare with the data in Vol. II, p. 154):

density (20/4) 1.230–1.234
boiling: do not start below 280°C,
90% distilled not over 295°C
moisture: no more than 0.5%
chlorides: traces
acids (H_2SO_4): no more than 0.02%
saponification as Na_2O: no more than 0.05%
reducing matters: none.

MANUFACTURE OF PENTAERYTHRITOL TETRANITRATE (PETN) (Vol. II, p. 185)

Relatively little can be added to the description of the methods of PETN manufacture. Continuous methods are mostly used in modern plants (see also Fig. 74, Vol. II, p. 188).

The nitration characteristics of pentaerythritol (PE) can be summarized as follows:

1. Use of low temperature of nitration with nitric acid (d 1.50),
2. Ease of separation of PETN from the spent acid by the fact that the product is a crystalline solid, and ease of washing it from the acid,

3. High sensitivity of PETN to impact which should always be kept in mind,
4. Instability of the spent acid.

Pentaerythritol (PE), 'nitration grade'. According to 'Biazzi SA' [18] PE should possess the following characteristics:

M.p.	263 ± 1°C
Humidity	max 0.2%
Crystal size	min dia. 0.025 mm max dia. 1.0 mm
Formic acid	absent
Dust	absent
Water insoluble parts	max 0.2%
Ashes	max 0.01%
Monopentaerythritol	96.5–98.5%
Dipentaerythritol	0.7–1.3%

The following is the description given by Biazzi SA [18] on the continuous nitration of PETN – Fig. 47 with two nitrators.

The dry pentaerythritol (PE) of specified granular size and quality (see the specification above) from (1) loaded into a feeding hopper (2) is fed into the first nitrator (3) by means of a vibrating system giving a constant flow rate. The feeder is provided with a variator making it possible to modify the feeding rate. Simultaneously a continuous flow of nitric acid (98.5% HNO_3) is introduced into the nitrator in the right proportion (5:1).

From the first nitrator the suspension of PETN nitric acid enters the second nitrator (4). The temperature 15–20°C is maintained by a freon filled jacket and controlled by the cooling agent valves. The nitric acid is fed into the first nitrator from a constant-level overhead tank (5). The contents of the nitrators are stirred by paddle type stirrers, driven by electric motors which are located outside the building or in a separate motor room. Gas from the nitrator is washed with water in a column (6).

Camera [19] discussed the control of the safety of nitration of pentaerythritol with nitric acid by Redox measurement as described in Chapter X.

The PETN suspended in the spent acid overflows from the second nitrator into a continuous vacuum filter (7). The spent acid goes through a filter into an intermediate vacuum tank equipped with a strainer retaining all the PETN which may escape from the filter. From the tank the acid is pumped to storage by means of a diaphragm pump controlled by a level switch in the intermediate vacuum tank.

From the filter PETN is transferred to the dissolution neutralization and crystallization equipment by a water jet. Although the nitration of Pentaerythritol (PE) should be regarded in itself as a relatively safe operation compared to the

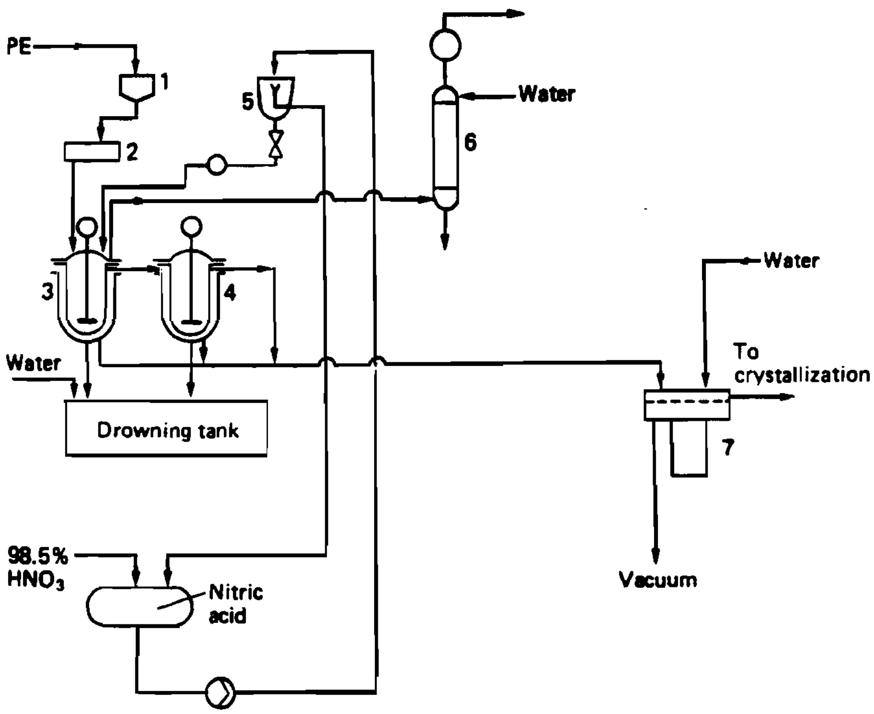

FIG. 47. Simplified flow sheet of Biazzi method of making PETN (Courtesy M. Biazzi S.A.)

nitration of glycerine and trinitration of toluene, there is a certain amount of danger particularly from the storage of spent acid for a longer time. This is the result of hydrolysis of PETN to lower nitrated PE, that is, PETriN and PEDN described by Camera [20]. The lower nitrated products can be relatively readily oxidized and this of course is manifested by the formation of nitrous acid.

One of the important requirements for the safety of nitration of PE is keeping the right proportion of nitric acid to PE (5:1).

A few accidents with PETN described by Biasutti [15] were very instructive. A typical accident happened through a faulty rotameter giving a wrong dosage of the acid in the continuous method of the manufacture of PETN. Insufficient quantity of the acid produced a considerable increase in the temperature in the nitrator and a violent decomposition of PETN [21].

The sensitivity of PETN to shock was the cause of another accident. This happened when the crust of the explosive was removed from the stirrer with a steel chisel. This was against the regulation which required the use of a solvent (acetone) and either wooden or plastic tools [22].

The storage of spent nitric acid is dangerous particularly in a concentration of 75–80% [23] or from other sources 65–75% [24]. The probable cause of the 'fume off' of the spent acid is hydrolysis of the lower esters followed by oxidation as described above.

However, Ramaswamy and Subba Rao [23] suggested a 'controlled fume-off' as a means of avoiding the danger of keeping spent acid. Two methods were recommended both by injecting live steam:

(1) keeping the temperature at 70 ± 2°C;
or (2) at 95–100°C with an additional injection of N_2 or air.

This is fully discussed in Chapter XIII dedicated to the treatment of spent acids.

Purification of PETN

The usual method for the purification of PETN consists in crystallization from acetone (Vol. II, pp. 188–189).

A description of crystallization as given by Biazzi SA [18] is as follows. PETN is continuously introduced from the filter into a stainless steel dissolving apparatus provided with a hot water heating jacket and a stirrer. The required amount of acetone is continuously fed from a constant-level overhead tank together with ammonia gas for neutralization. The neutralized solution of PETN in acetone flows continuously into a series of continuous crystallizers equipped with stirrers and jackets. The crystallization is carried out by adding a well determined quantity of water. The contents of the last crystallizer flow continuously on a continuous vacuum filter where most of the waste acetone is removed. The dilute acetone is collected into an intermediate vacuum tank from which it is pumped to the acetone recovery unit.

The moist and recrystallized PETN falls continuously from the filter into the containers for further use.

The plant is provided with an electro-pneumatic safety system which signals all emergencies during the operation and sets the automatic safety devices in action if the intervention of personnel fails.

The material balance of the Biazzi process is given below for 1000 kg of produced PETN [18]:

PE was used in quantity	450 kg
Nitric acid (as 100% HNO_3)	2250 kg (not including recovery)
Acetone *ca.*	300 kg
Ammonia (as 100% NH_3)	1.5 kg
Process water	12 000 l.

By-products and wastes:

Spent acid (81–84% HNO_3)	1650 kg for recovery

Acidic waters: 3750 kg which should be neutralized and sent to the drains.

Acetone (30%) water: 9250 kg to be sent to acetone recovery plant.

Specification of the final product (PETN).

M.P. min. 140°C
Abel heat test at 30°C: min. 30 minutes
Nitrogen content: min. 14.5%
Insoluble in acetone: max. 0.1%
Bulk density: max. 800 ± 80 g/litre
Acidity: max. 0.005% (HNO_3)
Ash: max. 0.05%
Water (for the safety in transportation and manipulation); max. 20%.

US standards have slightly different requirements.

According to Roth [25] PETN for military use in the USA shall correspond to data as below:

Melting point: 141° ± 1.0°C.
Nitrogen content: min. 17.5%
Acetone insoluble material: max. 0.10%
Acidity or alkalinity: max. 0.01%

120°C vacuum stability: the max. amount of gas evolved in a 20 hour test should not exceed 5 ml.

Granulation. PETN should comply with the granulation requirements shown on Table 57.

TABLE 57. Sieving of PETN (US specification)

US Standard Sieve No.	Percent Passing through the Sieve			
	Class 1	Class 2	Class 3	Class 4
30			95 min	100 min
80	100 min			
100	85 min	96 min		20 max
140	55 max			
200	30 max	80 max 65 min	30 max	

With regard to the safety of crystallization attention should be paid to the danger of explosive acetone–air mixtures which have been responsible for some accidents [26]. In some countries (e.g. Japan) purification of PETN is carried out by heating PETN with water in autoclaves in a manner similar to that for nitrocellulose (Vol. II, pp. 411–413). However, an explosion occurred when PETN was heated with 30% water in an autoclave [26]. The accident was probably produced by overheating.

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CHAPTER 12

CARBOHYDRATE NITRATES

CELLULOSE AND CELLULOSE NITRATES (NITROCELLULOSE)
(Vol. II, pp. 213, 234, 293, 321, 362, 393)

With regard to cellulose two more collective volumes have appeared [1] which are the continuation of the former ones edited by Ott, Spurlin and Graffin. However, most of the text is now dedicated to the biosynthesis of cellulose and modifications of cellulose which are outside the scope of the present book. Only one chapter written by Hiatt and Rebel [2] refers to esters of cellulose, including nitrocellulose and the information given by these authors is used in the present volume.

With regard to the present advances in the chemistry of cellulose an excellent review has been given by Shafizadeh [3]. He also refers to the folded chain structure of cellulose [4, 5] and of the structure of elementary fibrils [6].

Cellulose for nitration. In most European countries wood cellulose is now used for nitration (Vol. II, p. 364). The success of the nitration of cellulose from wood depends on a high proportion of α-cellulose in wood cellulose. According to Petropavlovskii, Krunchak and Vasilyeva [7] the yield of nitrocellulose highly depends on the α-cellulose content and can be proportional to this content. Some authors [8] consider that lower quality of nitrocellulose from wood-cellulose is due to the presence of hemi-celluloses (mainly pentosanes) in it.

Nevertheless wood cellulose has a lower molecular weight than cotton cellulose, which explains the lower molecular weight of nitrocellulose from wood. Some attempts have been made to produce a higher quality nitrocellulose from wood by carrying out the nitration in two stages, for example [9] but this technique did not seem to find a wider application although the semi-continuous method of nitration of Bofors-Nobel-Chematur (see p. 346, Fig. 48) includes the nitration in two stages:

(1) Pre-nitration,
(2) After-nitration.

Structure of Cellulose Polymer and Determination of Molecular Weight
(Vol. II, pp. 261–278)

The structure of cellulose has only relatively recently been tackled through the examination of its trinitrate, that is, nitrocellulose of *ca.* 14% N. Trinitrate of cellulose was chosen as a readily available cellulose ester, soluble in polar solvents, of an almost unique unbranched polymer chain structure having a broad range of molecular weights manifested by the degree of polymerization 250–9000.

Holtzer, Benoit and Doty [45] undertook the task of fractioning samples of nitrocellulose with 13.8–14.1% N. *n*-Hexane was added dropwise while stirring to 0.2% solution of nitrocellulose in acetone and several fractions were obtained. Their molecular weight was determined by light scattering, viscosity and osmotic pressure measurement.

Light scattering gave the following figures:

(1) Weight average molecular weight: $\bar{M}_n = 2\,640\,000–77\,000$
(2) Number average molecular weight: $\bar{M}_n = 1\,320\,000–4500$.

Thus the polydispersity $\bar{M}_w/\bar{M}_n$ is *ca.* 2. However most commercial samples of nitrocellulose have a high polydispersity: 2.5–3.5. (For the description of $\bar{M}_w$ and $\bar{M}_n$ and their calculation see [46].)

Measurement of viscosity gave lower figures. The above results were confirmed by Hunt, Newman, Scharaga and Flory [47]. Their figures for the molecular weight of fractions were lower: 575 000–40 000. Canadian workers [48] obtained figures of 2 500 000–650 000. Their method of fractionation consisted in adding water to the solution of nitrocellulose in acetone [49].

The conclusion from the above experiments was that:

(1) molecular weight of nitrocellulose (e.g. 400 000) is much higher than that of most vinyl synthetic polymers,
(2) the cellulose skeleton in nitrocellulose is manifested by an unusually stiff chain.

Both these characteristics are responsible for the very high viscosity of nitrocellulose solutions.

Recently British authors [50] described a simple method of determining number-average and weight-average molecular weight of 12.6% N pyro nitrocellulose. The measurement was made with a 3% solution in acetone/ethanol. The viscosity is related to the number-average and weight-average molecular weight. By adding *ca.* 7% lead β-resorcylate a fractional increase in the viscosity was found, which is a function only of number-average molecular weight. Once calibration has been made against osmotic pressure measurements and intrinsic viscosity, both number- and weight-average may be measured rapidly.

Pyrolysis of Nitrocellulose

Ettre and Varadi [51] examined pyrolysis of nitrocellulose (no nitrogen content was given) between 300° and 950°C. The decomposition yielded almost completely gaseous products: CO_2, CO, nitrogen oxides, CH_4, H_2O, lesser amounts of nitrogen (increasing with temperature) and small quantities (below 2%) of ethylene, acetaldehyde, methanol, ethanol and methyl acetate. The latter four compounds were not found at 900–950°C. A small solid residue which formed between 300° and 500°C yielded gaseous products above 500°C.

At 175–250°C a solid residue was produced which decomposed only partly to volatile products when heated to 600°C. This indicated the difference between the composition of products formed at 300–500°C and at 175–250°C.

Osada and Hara [53] examined the action of UV radiation on nitrocellulose and found that evolution of NO_2 and NO occurred. In oxygen atmosphere nitrocellulose absorbed oxygen which promoted denitration and depolymerization. Also salts of di- and trivalent iron promote depolymerization.

Thermochemical Properties of Nitrocellulose (Vol. II, p. 313)

The National Bureau of Standards [41] reported their results for determining heat of combustion and heat of formation of dinitrate- and trinitrate of cellulose (Table 58).

TABLE 58. Heat of combustion and formation of nitrocellulose [41]

Compound	Heat of combustion cal/g	Heat of formation cal/g
Cellulose Dinitrate	2614.4–2616 and 2606.0–2608.6	715.3–712.8
Cellulose Trinitrate	2190.7–2188.7 and 2179.5–2178.1	523.4–525.4

Nitration. As pointed out in Vol. II (p. 321) the only industrial method of nitrating cellulose consists in using a nitric acid–sulphuric acid nitrating mixture. The other nitrating mixtures, such as nitric acid/phosphoric anhydride, nitric acid/acetic anhydride, nitric acid/chlorinated hydrocarbons were in use occasionally on a laboratory scale to solve some problems connected with the nitration of cellulose. Thus Bennett and Timell [10] confirmed the work of Bouchonnet, Trombe and Petitpas (Vol. II, p. 344) that the nitration of cotton dust with a mixture of nitric acid–acetic acid–acetic anhydride (in proportion 43:32:25) at 0°C can yield fully nitrated cellulose, that is, cellulose trinitrate of 14.14% N.

Thinius and Thümmler [11] obtained highly stable nitrocellulose of 13.8–14.0% N by nitrating cellulose with solutions of nitric acid in chlorinated hydrocarbons (see Vol. II, p. 346).

With regard to the mechanism of the nitration of cellulose, two modes were suggested for the formation of esters of cellulose (Vol. II, pp. 239–242). One of the mechanisms suggests gradual introduction of NO_2 groups: at the beginning on the surface of micells followed by a step-wise deeper penetration. Another mechanism suggests simultaneous reactions of OH groups with nitric acid. The latter mechanism seems now to be accepted according to Hiatt and Rebel [2].

Sakata and Komatsu [12] used infra red and X-ray techniques to study the mechanism of the nitration of cellulose with nitric and phosphoric or sulphuric acid. Their conclusion can be summarized as follows. Nitric acid penetrates into crystallites and most OH groups simultaneously react with the reagent in the presence of phosphoric acid. In the presence of sulphuric acid the accessibility of OH groups gradually increases. The part of the molecule which has not reacted shows the same pattern as the original unnitrated micell.

Kunz, Kompolthy and Balogh [13] examined the trend of the nitration of mechanically pulverized cellulose. They found that the nitration obeys the same rule as the nitration of starch, reported by Kunz and Toth (Vol. II, p. 430). The same dependence: reaction time on the reaction temperatures exists in both cases and the degree of nitration plot on triangle diagram (Vol. II, pp. 333–336, 429) are identical, without the typical one phase system for nitrostarch due to the solution of starch in nitrating mixtures rich with nitric acid. A correlation exists between the activity of nitric acid (Vol. I, pp. 28–30) and the duration of the reaction. The reaction was fully accomplished in 8–13 minutes depending on the composition of mixed acids. It was found that the introduction of one NO_2 group into the cellulose molecule develops 1696 ± 85 kcal/mol. This figure consists of the actual heat of reaction of nitration and the heat of absorption of nitric acid by cellulose (see Vol. II, p. 358).

Mixed Esters: Nitrates and Sulphates

It is well known that the low stability of nitrocellulose is often attributed to the presence of sulphates of cellulose, usually in the form of mixed esters: nitrato-sulphates (Vol. II, pp. 293–298). A number of patents [1] have attempted to obtain nitrocellulose free of sulphates by nitrating cellulose with nitrating mixtures composed of nitric acid and salts of nitric acid, such as magnesium nitrate [14] much in the way described in Vol. II, pp. 346–347.

The analytical method of determining the quantity of sulphate groups in nitrocellulose was given by Dawoud, Saad an Attia [15] who used a quick analytical method of determining sulphate esters of cellulose:

(1) by the ignition of samples in a calorimetric bomb,

(2) by titrometric determination of sulphate using Thorin titration method with $BaClO_4$.

The conclusion of this important work is given here. Unstabilized samples of 12.2%, 12.52% and 13.3% N have shown 0.68%, 0.44% and 0.37% SO_4 respectively.

Finished commercial products showed only trace quantities of SO_4:

nitrocellulose of 12.2% from linters: 0.01%
nitrocellulose of 12.16% from wood cellulose: 0.02%
nitrocellulose of 13.2% from linters: 0.03% SO_4.

Attention should be drawn to the work of Castorina, Helf, Aaronson and Kaufman [52] who examined the nature and amount of sulphate present in nitrocellulose and mechanism of its removal during stabilization by using the radioactive tracer – sulphur 35. Thus nitrocellulose of 13.35% contained 0.84% sulphate. After 56 hours of boiling in acid it was reduced to 0.05%. The latter could not be removed. The authors concluded that *ca.* 90% of sulphate in unstabilized nitrocellulose is removable sulphuric acid and the remainder is sulphate ester which is difficult to remove.

Nitration of wood meal with N_2O_5 vapour at 0° to –2°C *in vacuo* was also described [16].

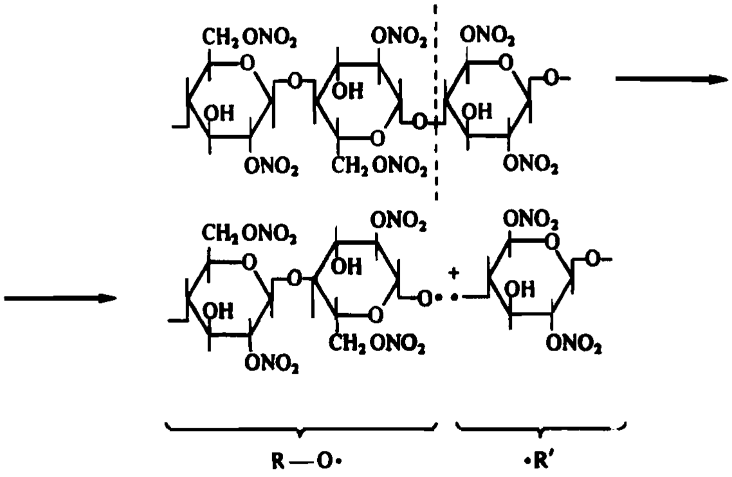
Stabilization of Nitrocellulose

As described in Vol. II, p. 393 stabilization comprises washing and boiling nitrocellulose in kiers (if necessary an additional kiering in autoclave), pulping in beaters or mills (refiners) followed by final boiling and washing.

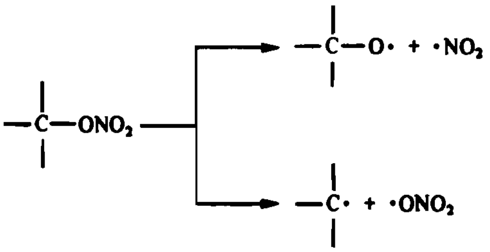
Hess and Trogus (Vol. II, p. 241) have shown that boiling nitrocellulose increases the regularity of the structure of the obtained molecule. A very important part of stabilization is pulping the nitrated fibres. Mechanical cutting of the fibres into shorter ones produces a depolymerization manifested by a decrease in the viscosity of the solutions of nitrocellulose (Vol. II, p. 276).

Steurer and Hess [17] have already calculated that the kinetic energy from the impact of balls (in a colloid ball mill used by Staudinger – Vol. II, p. 276) on cellulose fibres should be sufficient to rupture covalent bonds in cellulose such as C–C, C–O. Breaking such bonds requires energy of the order 80–90 kcal. This statement was substantiated by Swedish authors [18] who found experimentally that the covalent bonds in cellulose, as above, can be ruptured by mechanical action (in an agate ball mill). It has been known since 1895/96, thanks to the work of Bruley (Vol. II, p. 276), that pulping nitrocellulose reduces the viscosity of its solutions, but only now the experimental facts can be explained in terms of breaking the covalent bonds. This was done by T. Urbański

[19] who suggested a sequence of reactions given in scheme (1). First breaking a bond between pyrane ring can occur forming free radicals (a) RO· and R'·. Also a rupture of the bond $-C-O-NO_2$ can occur forming free radicals $-C\cdot$, $-C-O\cdot$, $\cdot ONO_2$ and $\cdot NO_2$ (b) All free radicals can react with water to yield: $R-OH$, $R'-OH$ and $-C-OH$, $-CH$, $HONO_2$ and HNO_2 (c)

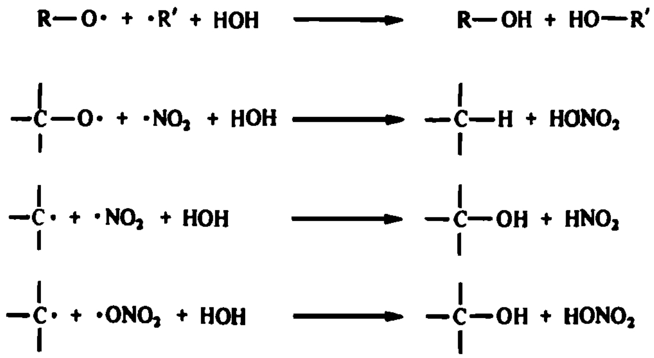


(1a)



$$-\overset{|}{\underset{|}{C}}-ONO_2 \longrightarrow \begin{cases} -\overset{|}{\underset{|}{C}}-O\cdot + \cdot NO_2 \\ -\overset{|}{\underset{|}{C}}\cdot + \cdot ONO_2 \end{cases}$$

(1b)



$$R-O\cdot + \cdot R' + HOH \longrightarrow R-OH + HO-R'$$

$$-\overset{|}{\underset{|}{C}}-O\cdot + \cdot NO_2 + HOH \longrightarrow -\overset{|}{\underset{|}{C}}-H + HONO_2$$

$$-\overset{|}{\underset{|}{C}}\cdot + \cdot NO_2 + HOH \longrightarrow -\overset{|}{\underset{|}{C}}-OH + HNO_2$$

$$-\overset{|}{\underset{|}{C}}\cdot + \cdot ONO_2 + HOH \longrightarrow -\overset{|}{\underset{|}{C}}-OH + HONO_2$$

(1c)

This scheme explains both the reduction of the viscosity and a slight denitration of nitrocellulose during the pulping (Vol. II, p. 276) and the presence of $Ca(NO_3)_2$ and $Ca(NO_2)_2$ in water in beaters. Calcium salts are being formed from calcium carbonate added to the water in the course of the work of beaters.

Degradation of polymers by mechanical action (tribo- or mechano-chemistry) is now generally accepted and has been described in two monographs [20, 21].

Knecht Compound

The structure of "Knecht compound" has been examined by T. Urbański and Żyszczyński [54]. On the basis of infra red spectra they came to a conclusion that the cellulose moiety of the Knecht Compound is partly oxidized and shows the presence of a carbonyl group similar to that of oxycellulose (Vol. II, p. 321).

Manufacture of Nitrocellulose. Continuous Methods

As pointed out in Vol. II, p. 391 numerous attempts have been made to introduce continuous methods of cellulose nitration. In addition to those mentioned in Vol. II, the following continuous methods were reported by Hiatt and Rebel [2]: Plunkett [22], Plunkett and McMillan [23], Reinhardt [24]. Ramsey [25] described a continuous method with nitric–phosphoric acid mixtures, and Bergman [26] – nitration of powdered cellulose. Diels and Orth [27] used spent acid for the first step of nitration followed by the second with fresh mixed acid.

Matasa and Matasa [28] described a number of continuous methods of cellulose nitration, among them patents by Hercules Co. [29] and Wasag Chemie [30].

So far none of the above methods have received practical application, and it appears that only two methods are in use on an industrial scale:

(1) semi-continuous method used by Bofors-Nobel-Chematur in Sweden and
(2) continuous method used by Hercules Powder Co.

The Semi-continuous Method of Bofors-Nobel-Chematur [31]

The method is depicted by Fig. 48. It was developed in the early 1960s at the Nobel Works, Karlskoga, Sweden. The process comprises continuous nitration, continuous centrifuging and batch stabilization.

Cotton, cotton linters or wood cellulose is made fluffy by a disintegrator and dried in a continuously working belt drier. Dried cellulose is continuously mixed with nitrating acid in a prenitrator. From there the mixture passes into a defibrator where very close contact is obtained between the cellulose fibres and the acid and all enters into an 'after-nitrator' where the nitration is completed.

The method of continuous centrifuging depends upon whether low or high-

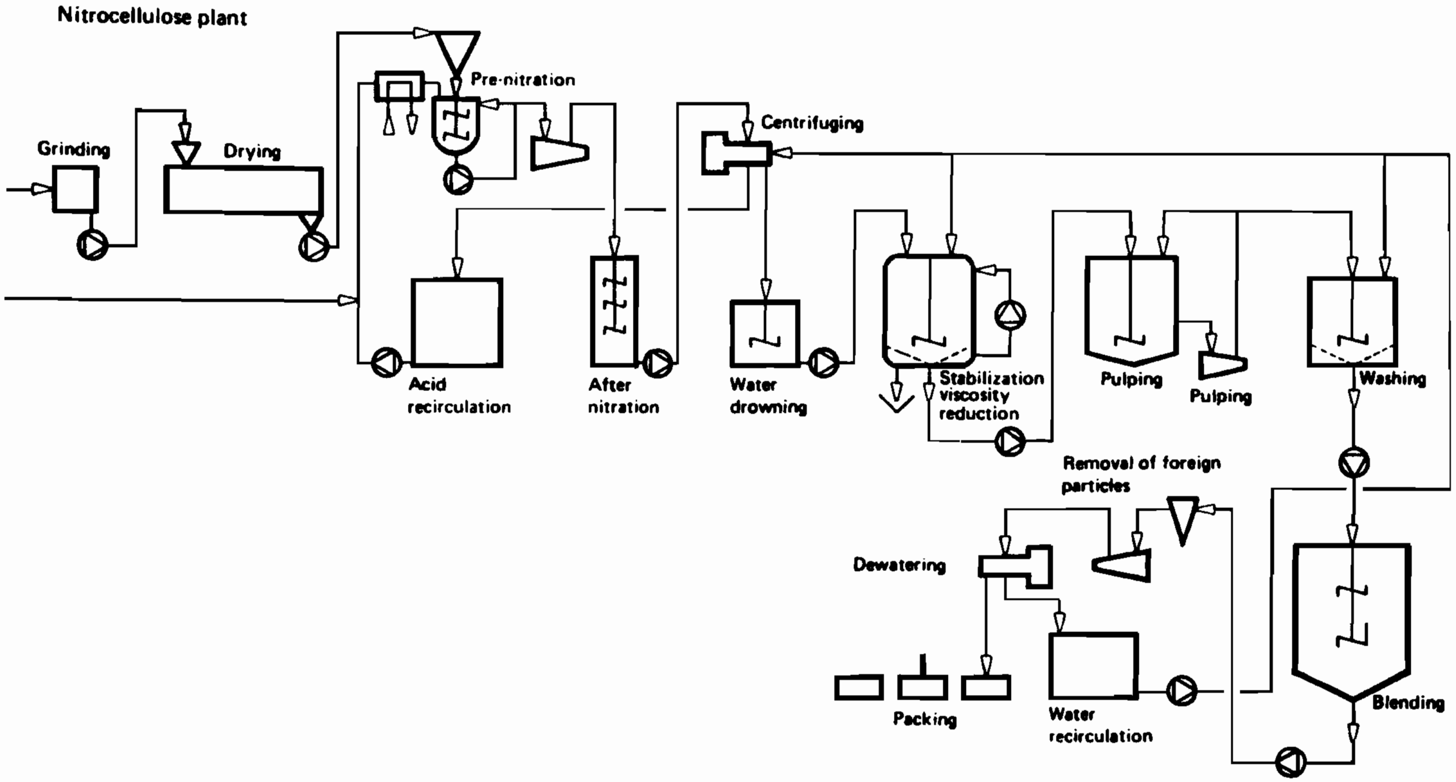


FIG. 48. Semi-continuous making of nitrocellulose of Bofors-Nobel-Chematur (Courtesy Bofors-Nobel-Chematur)

nitrated nitrocellulose should be obtained. Low-nitrated product continuously flows through three stages in the centrifuge. In the first stage the main part of the acid is removed, in the second stage the nitrocellulose is washed with dilute acid and in the third stage the nitrocellulose is washed with water. High-nitrated nitrocellulose is not washed with acid and water.

When leaving the centrifuge the nitrocellulose is mixed with water and pumped to stabilization. The spent acid is partly mixed with nitric acid and oleum for re-use and partly sent for denitration.

The nitrated cellulose is boiled in pressure kiers. The boiling time and temperature depends on the required quality of the product.

Kiered nitrocellulose is pulped in refiners (Fig. 49). The refiners are of the same design as Jordan mills. They contain a conical bar fastened on a movable shaft around the mantle equipped with knives. The inside of the conical shell is also equipped with knives. The nitrocellulose—water slurry is pumped through the gap between the knives. The gap between the knives is adjusted by moving the conical part horizontally.

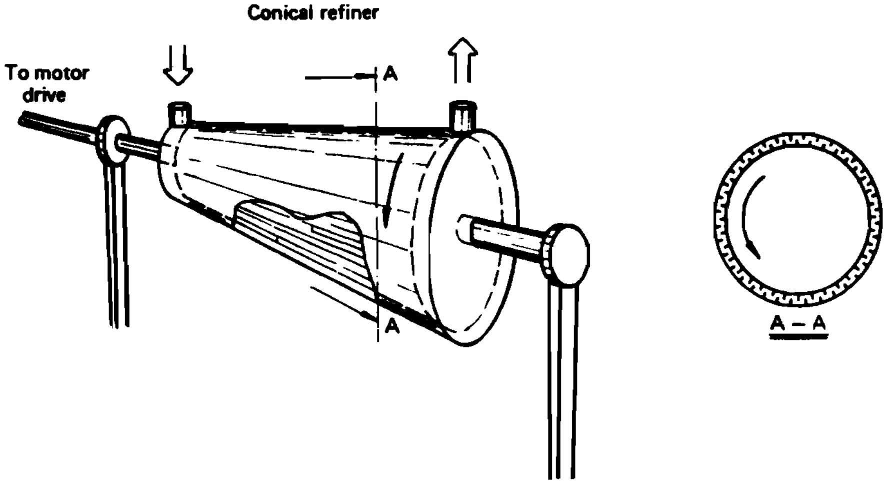


FIG. 49. Conical refiner (Courtesy Bofors-Nobel-Chematur).

Pulped nitrocellulose is subjected to the usual operations: further boiling, washing, blending and the removal of foreign particles. After that the nitrocellulose is dewatered in a centrifuge.

Diagram of Continuous Method of Hercules Powder Co. Ind. [32]. A continuous fully automatic nitrating method is shown in Fig. 50. Dried cellulose and mixed nitrating acid are introduced continuously to a nitration. A suspension of nitrocellulose in the acid enters a centrifuge. The centrifuge is the essential part of the system. It is divided into zones and nitrocellulose is advanced from one zone to another. In the first zone most of the original acid from the nitration is removed. In each of the succeeding zones the acid in nitro-

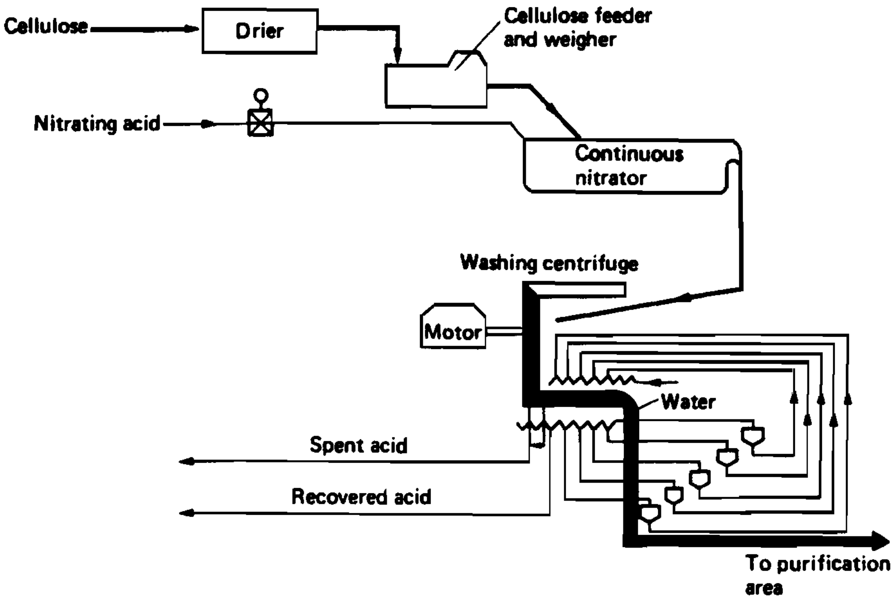


FIG. 50. Diagram of continuous method of making nitrocellulose of Hercules Powder Co.

cellulose is displaced with weaker acid and finally in the last zone – with water. In all zones the process occurs simultaneously. The water used for the final displacement is used for the preceding washing and so on, this is done in every step: each effluent is used for the preceding step. Subsequently the displacing acid leaving the system is composed of spent acid of nitration.

Hercules Co. points out that the product of the continuous nitration is more uniform than from the batch processes.

Drying Nitrocellulose

As is known nitrocellulose is stored and transported with 30% water or ethanol. It is also known that for a single base powder (nitrocellulose powder) water in nitrocellulose is replaced by ethanol which remains in it as an ingredient of the solvent (Vol. II, p. 573). However for some types of double base powder (cordite, Vol. III, p. 642) it is necessary to dry the nitrocellulose. Drying nitrocellulose is essential in the manufacture of dynamite (Vol. II, p. 511). However it has so far been considered the most dangerous operation with dry nitrocellulose considering its ease of ignition and burning, and sensitivity to impact and friction. Mario Biazzi S.A. use a Finnish method Finska Forcit [33]. The idea of the system is given in Fig. 51. It consists essentially in drying humid nitrocellulose with dry warm air which passes through the nitrocellulose from the top to the bottom.

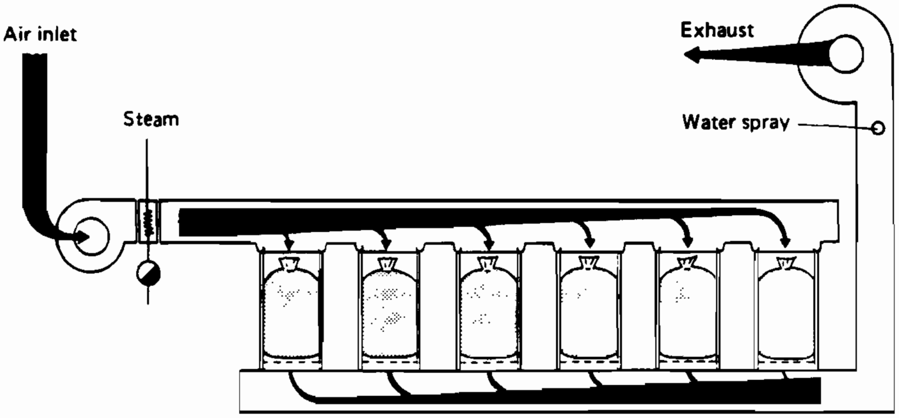


FIG. 51. Finska Forcit method of drying nitrocellulose (Courtesy M. Biazzi S.A.).

Moist nitrocellulose in cotton sacks is put in aluminium cylinders the bottoms of which are made of metal sieves, for example, of phosphorbronze wires. The thickness of the sheet of nitrocellulose should be 25–40 cm the diameter is chosen so that the content of one cylinder is used for one batch of dynamite. Dry air heated to 50°C enters the cylinders under pressure of 700 mm water. The amount of air is 30–50 nm^3 per kg of dry nitrocellulose.

The end of drying is manifested by the increase above 20°C in the temperature of the air leaving the cyclinders. To avoid the danger created by static electricity all cylinders should be earthed. Drying is ended after 1–2 hours. One of the advantages of the method is the fact that no nitrocellulose dust is formed.

Safety in the Manufacture of Nitrocellulose

Generally speaking the manufacture of nitrocellulose should be regarded as a relatively safe process. The most dangerous operation is drying nitrocellulose [34]. It also causes the largest number of accidents [35]. The explosions occurred mainly through the shock, overheating or discharge of static electricity. Another dangerous part of the work is centrifuging – the danger connected with it has been described in Vol. II, pp. 407, 380. Stabilization in autoclaves, that is, boiling nitrocellulose under pressure, also ended with explosions probably due to an insufficient quantity of water in the autoclave. As a consequence decomposition began with the increase of the temperature to 160°C and a violent reaction occurred.

STARCH NITRATES (NITROSTARCH) (Vol. II, p. 418)

Attention should be paid to Abdel-Rahman Shalash [36] who nitrated both amylose and amylopectin and gave an extensive review of the literature on nitrostarch.

Here are the main points of Shalash's work.

Nitration of amylose. This was achieved by using a nitrating mixture of nitric acid and acetic anhydride in volume proportions 50:50 and 60:40. Table 59 gives the main results.

TABLE 59. Nitration of amylose with HNO_3 : acetic anh. 60:40 after 24 hours [36]

Ratio Amylose:Acid	Temperature °C	%N in the product
1:10	10	13.4
	20	13.5
	30	13.66
1:25	10	13.5
	20	13.7
	30	13.76
1:50	10	13.6
	20	13.7
	30	13.8

Nitration of amylopectine. The nitration was carried out with nitric acid in the presence of pyridine. The nitration is extremely fast and the esterification equilibrium is reached at a relatively low degree of nitration as denitration intervenes.

Using nitric acid: pyridine ratio 70:30 and amylopectine: (nitric acid–pyridine) = 1:50 at 10°C, the product contained:

after one hour	11.45%N,
after two hours	12.25%,
after three hours	12.7%,
after four hours	12.1%.

Among other published papers on nitrostarch is that of Vollmert [37]. He nitrated starch with N_2O_5 vapour and obtained the product with 9.7–10.0% N.

X-ray analysis was carried out simultaneously with Kołaczkowska and T. Urbański (Vol. II, pp. 422–423) by Berl and Kunze [38] and by Centola [39]. The former authors examined both: amylose nitrate and amylopectine nitrate.

NITRATES OF VARIOUS CARBOHYDRATES

The thesis of Delpy [40] should be mentioned. He described the nitration products as follows:

hydrocellulose nitrate, 12.61% N

D-glucose nitrate	15.99% N (a sticky, soft substance),
D-mannose nitrate	15.40% N (as above),
D-fructose nitrate	13.56% N, crystals, m.p. 50–60°C,
saccharose nitrate	14.54% N, solid
maltose nitrate	12.03% N,
raffinose nitrate	14.36% N.

The nitration was carried out with a mixture of nitric acid (43.4%), sulphuric acid (44.25%) and water (11.85%).

POLYVINYL NITRATE (Vol. II, p. 173)

Efforts are being made to find an explosive polymer with properties similar to those of nitrocellulose. Naturally attention was directed towards the nitration of polyvinyl alcohol as the most accessible high molecular polyhydroxyl alcohol. It is described in the chapter dedicated to explosive polymers (Chapter XIV).

NITRO-DERIVATIVES OF LIGNIN (Vol. II, p. 433)

Attention is drawn to the monograph by Brauns and Brauns [42]. Although published in 1960 it contains a description of the main work on nitration of lignin.

The diagram suggested by Fraudenberg (Vol. II, p. 435) with the nitration of aromatic ring has generally speaking been confirmed.

The most important seem to be the paper published by Lieser and Schaack [43], Ivanov, Chuksanova and Sergeeva [44].

The form using the nitrating mixture with 7.4% water at 20°C yielded the product containing 12.2% N [43]. The latter nitrated lignin with nitric acid–phosphoric acid and nitric acid–acetic anhydride and obtained the product with 7.5% N [44].

No practical application has been found for the products of nitration.

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CHAPTER 13

N-NITRO COMPOUNDS

(*N*-nitramines and *N*-nitramides (Vol. III, p. 1)

This important group of explosives has recently received particular attention due mainly to heterocyclic nitramines–Cyclonite (RDX) and Octogene (HMX). Interest has also been maintained in Nitroguanidine and EDNA.

Several reviews on nitramines have appeared: by McKay [1], G. F. Wright [2] who reviewed the methods of formation of the nitramino group and its properties, Fridman, Ivshin and Novikov [3] who reviewed chemistry of primary aliphatic nitramines.

Darnez and co-workers [193, 194] revealed the formation of free radicals from secondary nitramines as the result of γ and ultra-violet radiation. Recently Dubovitskii and Korsunskii [4] have reviewed nitramines from the point of view of the kinetic value of their thermal decomposition and came to the conclusion of free radical-chain reaction of breaking the $N-NO_2$ bond. Also a monograph on octogen has appeared [5].

STRUCTURE AND CHEMICAL PROPERTIES

Very little can be added as regards the electronic spectra of nitramines (Vol. III, p. 3). Among earlier papers were those of Kortüm and Finckh [6], Mehler [7]. The latter author reported two maxima for Cyclonite in ethanol: 202 nm and a shoulder at 236 nm. Piskorz and T. Urbański [8] found the maxima at 232 nm. Two maxima 218–224 and 262–266 nm were present when the molecules contained other chromophores: C=O and C=NH in nitrourea and nitroguanidine (see also Vol. III, p. 25).

Infra red spectra [8, 9] were reported to show the frequencies:

NO_2 ν_{asym}	1630–1550 cm^{-1}
NO_2 ν_{sym}	1354–1262 cm^{-1}
N–N in primary nitramines	1000–948 cm^{-1}

See also the frequencies of *N*-nitrosamines [10].

In primary nitramines the frequency NH can be lowered to 3253–3240 cm^{-1} through hydrogen bonds between NH and NO_2 of neighbouring molecules or neighbouring groups in dinitramines. In deuterated compounds it can be lowered to 2400 cm^{-1} [11].

Primary nitramines are weak acids, for example, methyl nitramine shows pK_a = 6.0 [3].

The dissociation constants of *N*-nitro derivatives of α, ω-dinitramines also indicate their weak acid properties [12].

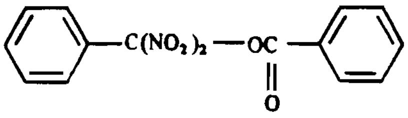
Nitrimino compounds containing $=N-NO_2$ should also be included in the group of compounds belonging to nitramines and nitramides.

On the contrary a *N*-nitro derivative of hydrazine, the nitroimide (I) (obtained by dehydration of quaternary nitrate of substituted hydrazine) possesses weak basic properties (pK_a = —4.2 ± 0.1) as shown by Epsztajn and Katritzky [13]:

$$(CH_3)\overset{+}{N}-NH_2\ NO_3^- \xrightarrow[-H_2O]{Ac_2O} (CH_3)_3\ \overset{+}{N}-N{=}NO_2^-$$

I

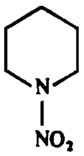
It should be pointed out that considerable effort has been made to obtain *N*-nitrohydrazine from unsubstituted hydrazine. The existing descriptions in the literature [66—69] cannot be considered as conclusive. Thus the nitration of *N,N'*-dibenzoylhydrazine did not yield *N,N'*-dinitrodibenzoylhydrazine [69] but an unsymmetrical αα-dinitrobenzoyl benzoate (II):



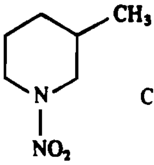
II

This was revealed by Lamberton and Harper [70].

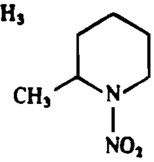
Chiral nitramines – derivatives of piperidine show an optical activity according to Ferber and Richardson [14]. Symmetrical compound III is non-chiral, asymmetrical compounds IV and V are chiral and optically active:



III

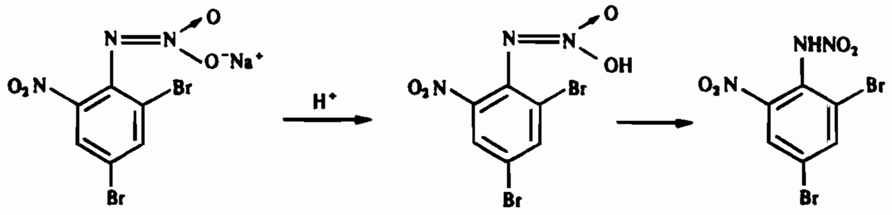


IV



V

The disputed existence of unstable aci-form of primary nitramines (Vol. II, p. 4) seems to be substantiated by Orton as early as 1902 [15]. Acting with alkalis on 2,4-dibromo-6-nitro-phenyl-1-nitramine he obtained a sodium salt which on acidification yielded a colourless unstable aci-product VI which was quickly transformed into the orange nitramine VII:

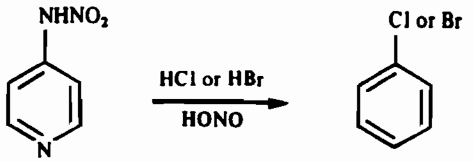


VI

Orange
m.p. 91-92°C

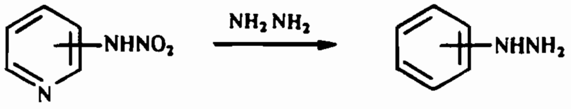
VII

The nitramine group attached to the pyridine ring can readily be replaced by halogen while acting with nitrous acid and hydrochloric or hydrobromic acid [16, 17]:

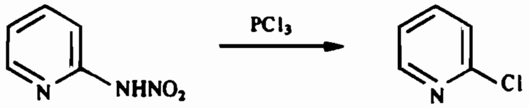


(1)

Talik and his co-workers succeeded in replacing the nitramino group with different nucleophiles (2) and (3) [18, 19]:



(2)



(3)

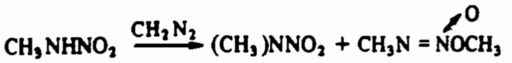
Nitramines can react with acids (Vol. II, p. 4). With hydrochloric acid the reaction can lead to the formation of chlorides and N_2O according to Lamberton and co-workers [20]:

$$\mathrm{R\,NHNO_2 + HCl \longrightarrow RCl + N_2O + H_2O.} \qquad (4)$$

The reaction can be used to reveal the presence of the $NHNO_2$. Nitrous acid can yield diazomethane while reacting with methylnitramine [21].

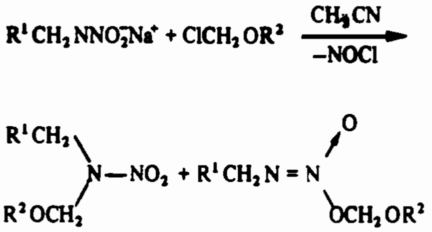
Nitramines are stable to bases at moderate temperatures, although some of them decompose readily (Vol. II, p. 6).

Primary nitramines can be methylated with diazomethane yielding both *N*-methyl and *O*-methyl derivatives [21] (5):



$$CH_3NHNO_2 \xrightarrow{CH_2N_2} (CH_3)NNO_2 + CH_3N = \overset{\nearrow O}{N}OCH_3 \qquad (5)$$

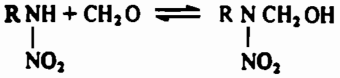
The reaction of nitramines with α-halogenoethers was studied by Thamer and Unterhalt [22] (6):



(6)

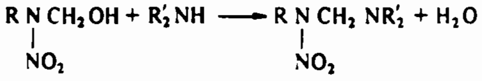
The same authors described a different trend of the reaction with α-halogenothioethers [23].

Primary nitramines react with formaldehyde to yield *N*-hydroxymethyl compounds. The reaction is reversible [24]:



$$\underset{NO_2}{RNH} + CH_2O \rightleftharpoons R\underset{NO_2}{N}CH_2OH \qquad (7)$$

The next step is the Mannich reaction (8) [24] which (as pointed out by Wright [2]) was carried out with nitramines by Franchimont [25] earlier than the work of Mannich:

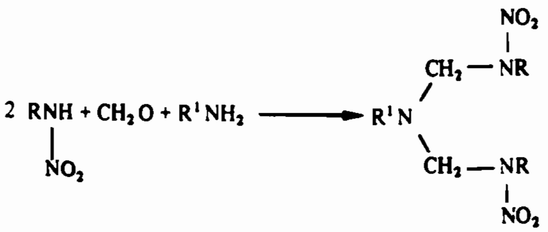


$$R\underset{NO_2}{N}CH_2OH + R'_2NH \longrightarrow R\underset{NO_2}{N}CH_2NR'_2 + H_2O \qquad (8)$$

VIII

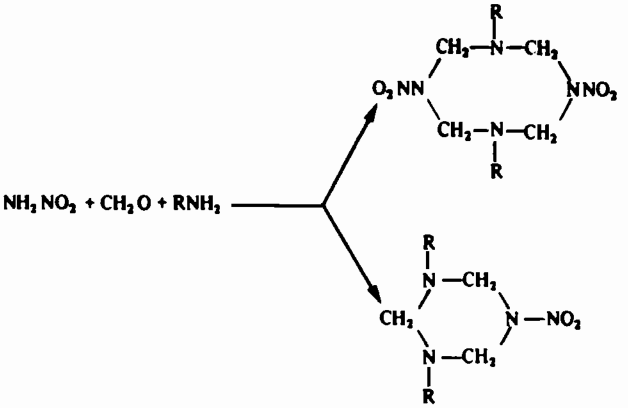
Bases VIII are soluble in water and split CH_2O through the action of alkalis, contrary to Mannich bases which are insoluble in water and stable towards alkalis.

By using primary amines R NH_2 Chapman, Owston and Woodcock [26] obtained nitramines with two nitro groups (9):



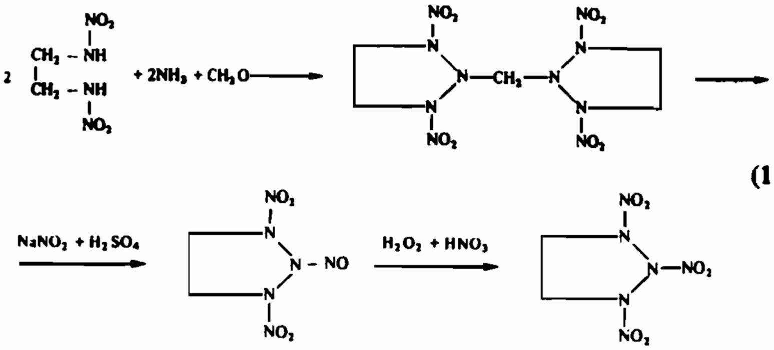
(9)

Also the same authors obtained cyclic nitramines by reacting nitramine (NH_2NO_2) (10) or primary dinitramines with primary amines:

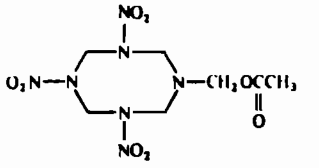


(10)

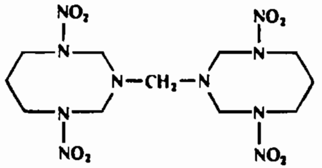
A wide range of cyclic nitramines through the reaction of dinitramines with formaldehyde and diamines were obtained and studied by Bell and Dunstan [27] and Novikov and co-workers [28]. Bell and Dunstan reported reaction (11) and formation of compounds IXa, b, c:



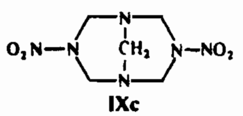
(11)



IXa



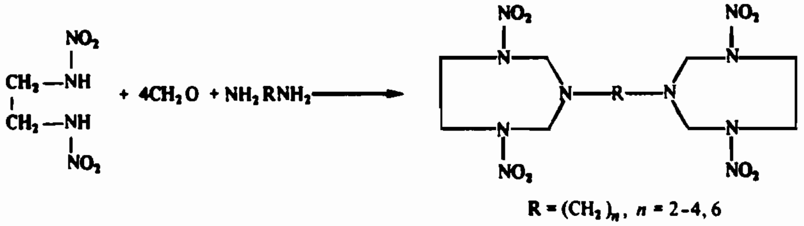
IXb



IXc
DPT
(Vol. III, p. 90, XII)

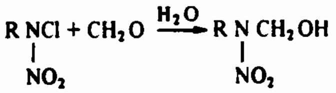
The nitrate salt of IXc was described by Stefaniak, Urbański, Witanowski, Farminer and Webb [196] among different other 3,7-disubstituted derivatives of 1,3,5,7-tetraazabicyclo-[3.3.1]-nonane. They examined their conformation by using NMR technique and came to a conclusion that they exist in either chair–chair or flattened chair–chair conformation.

Novikov *et al.* [28] described a number of cyclic products from the reactions:



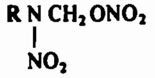
(12)

Formaldehyde can replace chlorine in *N*-chloro-*N*-nitramines to form an alcohol [29]:



$$R\underset{\substack{|\\ NO_2}}{N}Cl + CH_2O \xrightarrow{H_2O} R\underset{\substack{|\\ NO_2}}{N}CH_2OH \qquad (13)$$

The alcohols can be nitrated to yield *O*-nitro *N*-nitro compounds (X)



$$R\underset{\substack{|\\ NO_2}}{N}CH_2ONO_2$$

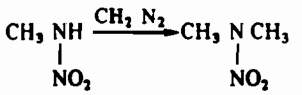
X

According to Majer and Denkstein [30] such esters are unstable, can readily decompose and are dangerous on storage.

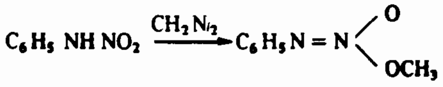
Acylation of primary nitramine occurs with great difficulty. Acetyl chloride can acetylate potassium or silver salts of primary nitramines with a yield according to White and Baumgarten [31]. It is rationalized that the difficulty of acetylating metal salts of primary nitramines comes probably from the assumption that the metal salts of nitramines are chelate compounds and not true salts.

Salts of nitramine can react with fluorine to yield fluoronitramine, for example, $C_4H_9\underset{\substack{|\\ NO_2}}{N}F$ [32].

Among other different reactions of primary nitramines alkylation should be mentioned. Methylation can be carried out with diazomethane and can yield methylated products at both: nitrogen (14) and oxygen (15) [33, 132]:

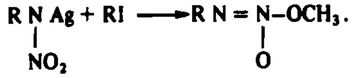


$$CH_3\underset{\substack{|\\ NO_2}}{NH} \xrightarrow{CH_2N_2} CH_3\underset{\substack{|\\ NO_2}}{N}CH_3 \qquad (14)$$



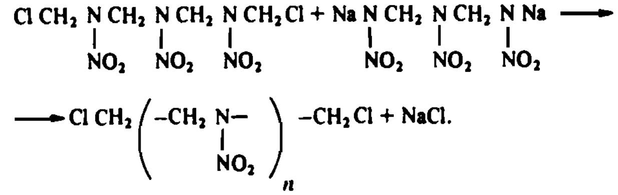
(15)

Alkylation can also be carried out with alkyl halides and dimethylsulphate. As a rule *O*-nitro derivatives are being formed [34], viz. (16):



$$R\underset{NO_2}{\underset{|}{N}}Ag + RI \longrightarrow RN=\underset{O}{\underset{|}{N}}-OCH_3. \qquad (16)$$

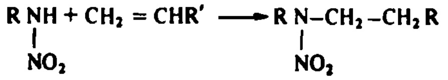
Potassium and sodium salts of primary nitramines react with compounds containing active chlorine, for example picryl-*N*-chloride and potassium methylnitramine yielded tetryl [35]. An interesting application of this reaction is the formation of a polymer from disodium salts of dinitramines and bis-*N*-chloromethylnitramines [36]:



$$ClCH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2Cl + Na\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}CH_2\underset{NO_2}{\underset{|}{N}}Na \longrightarrow ClCH_2\left(-CH_2\underset{NO_2}{\underset{|}{N}}-\right)_n-CH_2Cl + NaCl. \qquad (17)$$

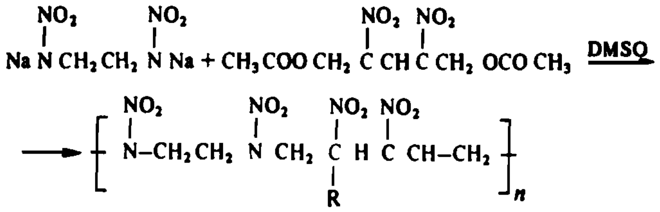
The polymer was suggested as a rocket propellant.

An important reaction is the addition of primary nitramines to an active double bond. This was reported by Kissinger and Schwartz [37] for example (18):



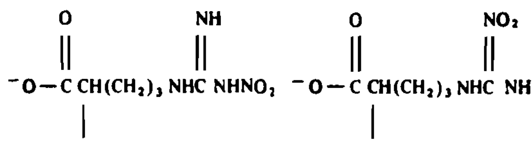
$$R\underset{NO_2}{\underset{|}{N}}H + CH_2=CHR' \longrightarrow R\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2R \qquad (18)$$

The addition of α, ω-dinitramines to the products of decomposition of nitrodiol acetates was described by Feuer and Miller [38]. The reaction (19) yielded a polymer:



$$Na\overset{NO_2}{\overset{|}{N}}CH_2CH_2\overset{NO_2}{\overset{|}{N}}Na + CH_3COOCH_2\overset{NO_2}{\overset{|}{C}}CH\overset{NO_2}{\overset{|}{C}}CH_2OCOCH_3 \xrightarrow{DMSO} \left[\overset{NO_2}{\overset{|}{N}}-CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2\underset{R}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}H\overset{NO_2}{\overset{|}{C}}CH-CH_2\right]_n \qquad (19)$$

The *N*-nitro protective group of arginine (XIa) was used in synthesis of peptides [39, 40]



$$^{-}O-\overset{O}{\overset{\|}{C}}\underset{NH_3^+}{\underset{|}{CH}}(CH_2)_3NH\overset{NH}{\overset{\|}{C}}NHNO_2 \qquad ^{-}O-\overset{O}{\overset{\|}{C}}\underset{NH_3^+}{\underset{|}{CH}}(CH_2)_3NH\overset{NO_2}{\overset{\|}{C}}NH_2$$

XIa XIb

According to N^{15}-NMR in aqueous solution it has nitrimine structure (XIb).

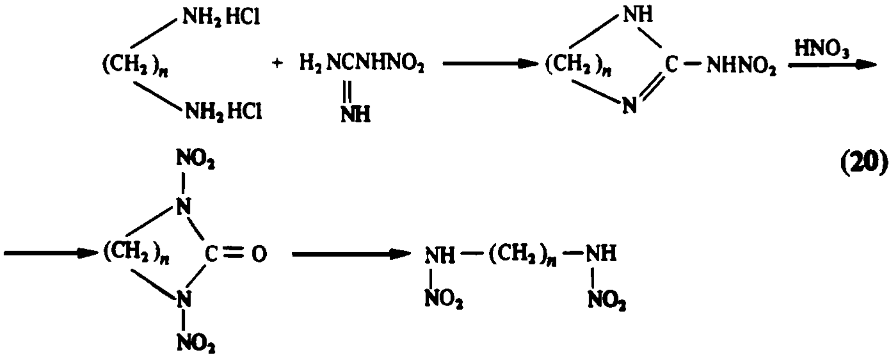
Naturally occurring nitramines have also been described, for example, *N*-nitroglycine [41] and β-nitroaminoalanine [42].

PREPARATION OF NITRAMINES

The methods described in Vol. III, p. 8 remain valid. The only addition related to the formation of dinitramines is given below.

Formation of Dinitramines from Nitroguanidine

This original method was described by McKay and Wright [43] and McKay and Manchester [44]. The method consists in reacting diamines with nitroguanidine to form cyclic products, which after nitration and hydrolysis produced dinitramines (20):



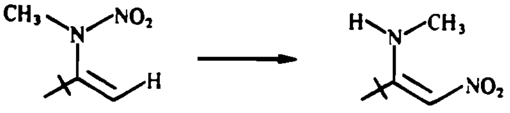
(20)

By this method 1,2-dinitraminopropane, 1,3-dinitraminobutane and 1,3-diamino-2-nitroxypropane were obtained. For more reactions of nitroguanidine see review [3].

N-NITROENAMINES

Some of this group of compounds can be subjected to an interesting 1,3-rearrangement of *N*-nitroenamines to *C*-nitro compounds according to Büchi and Wüest [71].

A simple refluxing of *N*-nitroenamine in xylene under an atmosphere of argon gave the reaction (21):



(21)

ALIPHATIC NITRAMINES AND NITRAMIDES (Vol. III, p.15)

Nitramine (Nitramide)

NH_2NO_2

m.p. 72–73°C

Nitramine offered a considerable interest owing to the simplicity of its molecule (the simplest *N*-nitro compound).

Acid and base catalysed decomposition of NH_2NO_2 has already been described by Hammett [45] who also mentioned earlier works such as that of Brønsted and Pedersen [46]:

$$NH_2NO_2 \xrightarrow{\text{Base}} N_2O + H_2O. \qquad (22)$$

Marlies and La Mer [47] confirmed their results.

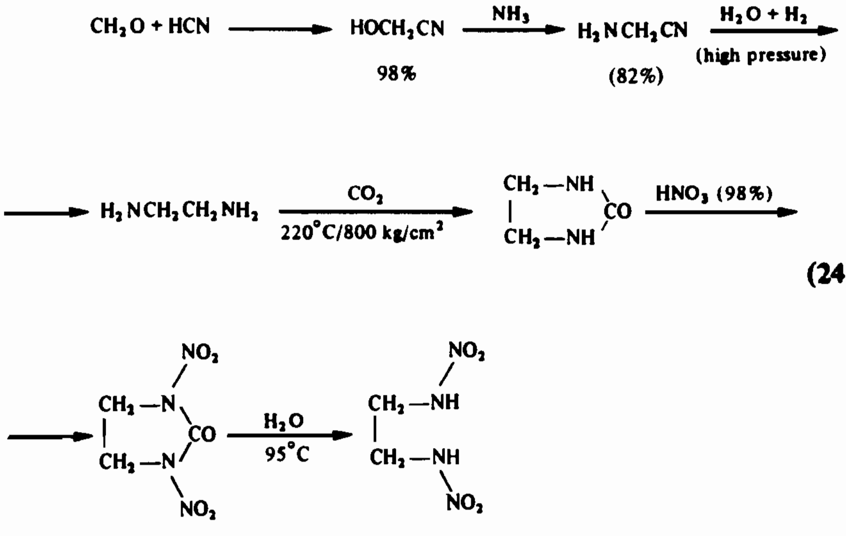
A wide examination of the base-catalysed decomposition of NH_2NO_2 was given by Kresge and co-workers [48, 49]. They suggested two parallel decomposition pathways:

$$B{+}NH{\cdot}NO_2H \rightleftharpoons BHN\,NO_2H \rightleftharpoons \overset{+\,-}{BHN}\,NO_2H \rightleftharpoons BH^+ + N_2O + OH^-. \qquad (23)$$

ETHYLENE DINITRAMINE (EDNA, HALEITE) (Vol. III, p. 18)

Preparation. Among different methods of preparing EDNA the method of Franchimont and Klobbie (Vol. III, p. 18) was repeated [50] by boiling dinitroethylenediurethane with alcoholic ammonia followed by acidifying the solution with hydrochloric acid with an overall yield of 60%.

According to American sources issued in 1971 [51] the full method of making EDNA consists in the following steps:



(24)

EDNA

For nitration fuming nitric acid was used and the overall yield was 70% which made the product reasonably cheap.

Physical and Chemical Properties

Pure EDNA has a m.p. of 177–179°C but begins to decompose at 175°C.

Structure by X-raying was determined by Llewellyn and Whitmore [52]. Atomic centres are confined (according to this analysis) to laminae paralleled to (001) approximately of 1.72 Å in thickness. The length of bonds are: NO 1.21 Å (as in nitromethane), C–C 1.52 Å, C–N 1.41 Å, N–N 1.33 Å. The short N–N bond is probably due to positive charges on both N atoms, as has been previously pointed out [11].

Specific gravity of crystals is 1.71 and the density of the pressed substance is:

at 350 kg/cm^2	1.28
700	1.38
1000	1.44
1400	1.49
2800	1.56

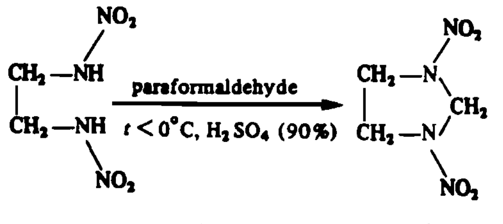
The solubility is given in Table 60.

TABLE 60. Solubility of EDNA

Temperature °C	Solvent Water	Ethanol
20	0.25	1.00
40	0.75	2.46
60	2.13	5.19
78	–	10.4
80	6.38	–
100	20	

The action on metals has also been described [51]: dry EDNA did not attack copper, brass, aluminium, mild steel, stainless steel, nickel, cadmium or zinc, whereas wet EDNA strongly attacked all the above metals with the exclusion of stainless steel.

EDNA is reactive owing to the presence of two primary *N*-nitro groups and according to Goodman [53] can readily form the imidazol ring:



(25)

EDNA is decomposed by hot dilute sulphuric acid (Vol. II, p. 20) and 20% NaOH [51].

Explosive Properties

EDNA is an exceptional, very strong, high explosive which is not very sensitive to impact but has a relatively low ignition temperature.

Thus initiation temperature is:

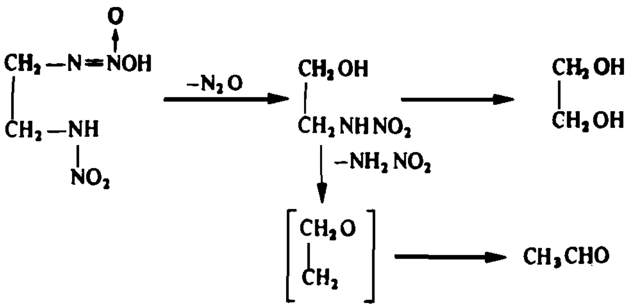
175°C after the induction of 5 sec. [54]
or 189°C after the induction of 5 sec.
216°C after the induction of 1 sec. [51]
265°C after the induction of 0.1 sec.
and 202°C on the basis of the differential thermal analysis [55].

The sensitivity to impact is similar to that of TNT.

Tomlinson [56] examined the decomposition of EDNA in water, dilute sulphuric acid and TNT at different temperatures: 60–120°C and 120°C respectively. EDNA is only sparingly soluble in molten TNT (*ca.* 5% solubility), but the rate of the decomposition much increased in the solution. EDNA in solution decomposed by a second order mechanism with the activation energy E = 20–35 kcal/mol. High acidity favours a low value of E.

In the solid state the decomposition follows a chain mechanism with E = 40–50 kcal/mol.

EDNA decomposes principally through the aci-form to yield glycol, acetaldehyde and nitrous oxide, probably according to the scheme (26):



(26)

Heat of combustion [57] was found to be – −2464.6 kcal/kg.

Heat of formation at C_v is −148 kcal/kg and at C_p −176 kcal/kg [58]. Heat of explosion 1276 kcal/kg and volume of gases 908 l/kg [51].

The explosive properties according to Ficheroulle [50] were: the velocity of detonation at the densities

1.15	6105 m/3
1.25	6800
1.35	7130

and lead block test 129% of picric acid, and Enclycopedia [51] gives for the velocity of detonation 7570 m/s for pressed, unconfined charge of 25.5 mm diameter.

Ficheroulle also described mixtures of EDNA with ammonium nitrate. The stoichiometric mixture of 42.8% EDNA and 57.2% NH_4NO_3 gave the velocity of detonation 6185 m/s at density 1.35 and lead block 113.5% of picric acid.

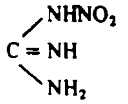
Specificiation of EDNA for US Army of 1943, amended 1947 [51] is as follows:

Moisture:	0.1% max.	
Colour:	white or buff	
M.P.:	174°C min.	
Purity (by dissolving in aqueous NaOH):	99% min.	
Insoluble matter (by dissolving in boiling water):	0.1% max.	
Granulation:	US Standard Sieve No. 10	100% min
	US Standard Sieve No. 100	20% max.

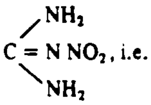
NITROGUANIDINE

Nitroguanidine became an important ingredient of treble base powder containing nitrocellulose–diglycoldinitrate–nitroguanidine (Vol. III, p. 664).

Nitroguanidine was subjected to some theoretical work, such as that dedicated to elucidating the structure:



and



, i.e. nitramino and nitrimino forms respectively.

X-ray analysis carried out by Bryden and co-workers [59] favoured the nitrimino form. Also NMR analysis of Richards and York [60] showed that the solid nitroguanidine exists in the imino form. Owen [61] calculated the MO of several compounds containing nitrogen and among them nitroguanidine and came to the conclusion that the calculated imino form fits better to the experimental values, as shown in Table 59, with the diagram of bond lengths. The imino structure was also confirmed by Kumler and Sah [62] measurement and calculation of dipole moment.

It is currently accepted that in the solid state nitroguanidine is in the imino-form, but in a solution both forms are present and are in the equilibrium [63]. Kemula and his co-workers [64] examined the change of the ultraviolet absorption spectrum with the change of pH. The spectrum so far published revealed two maxima in aqueous or acid solution: 210 and 265 nm (Vol. II, p. 25, Fig. 4). Kemula *et al.* found 246 and 264 nm. The same frequencies are in the alkaline medium of pH = 2–12, but in the solution of 1.5 M NaOH the longer wave absorption disappeared and the shorter wave band gains intensity (Fig. 52, Vol. III).

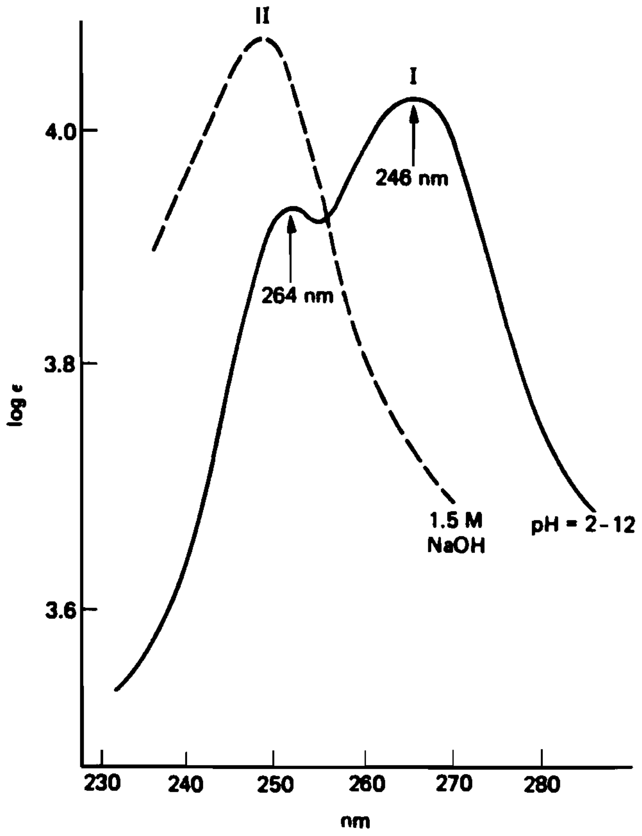
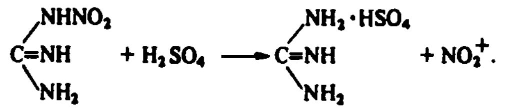


FIG. 52. Ultraviolet spectra of nitroguanidine (see Vol. III, p. 25, Fig. 4).

Reactions of Nitroguanidine

Very little can be added to the description of the chemical properties of nitroguanidine described in Vol. III, p. 25. Some of the reactions with nitroguanidine leading to dinitramine were given on p. 361.

Nitroguanidine in concentrated sulphuric acid can be used as a nitrating agent through the reaction:



$$\begin{matrix} \diagup^{\mathrm{NHNO_2}} \\ \mathrm{C{=}NH} \\ \diagdown_{\mathrm{NH_2}} \end{matrix} + \mathrm{H_2SO_4} \longrightarrow \begin{matrix} \diagup^{\mathrm{NH_2 \cdot HSO_4}} \\ \mathrm{C{=}NH} \\ \diagdown_{\mathrm{NH_2}} \end{matrix} + \mathrm{NO_2^+}. \qquad (27)$$

Anthraquinone was nitrated to 1,5-dinitro-anthraquinone by T. Urbański and Zyłowski [65]. The temperature of nitration was 110–120°C for 1 hour and the yield 67%.

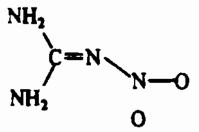
Specification according to Meyer [72]

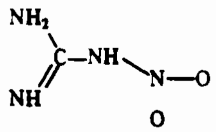
The existing specifications describe nitroguanidine as a white, free flowing crystalline powder of two types. Both types should correspond to the following requirements:

Ash content	0.30% max.
Acid content (as H_2SO_4)	0.06% max.
Volatile matters	0.25% max.
Sulphates	0.20% max.
pH	4.5–7.0
Type I	
grain size	4.3–6.0 μ
net content	min. 98%
Type II	
grain size	3.3 μ max.
net content	min. 99%.

TABLE 61. Nitroguanidine (bond length)

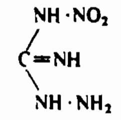
Bond	Nitrimino Form (I) Theor.	Nitrimino Form (I) Exper.	Nitramino Form (II) Theor.	Nitramino Form (II) Exper.
C–NH_2	1.36	1.36	1.37	1.36
C–N	1.35	1.34	–	–
C–NH	–	–	1.32	1.36
C–NH	–	–	1.38	1.34
N–N	1.29	1.35	1.31	1.35
N–O	1.23	1.22	1.22	1.22

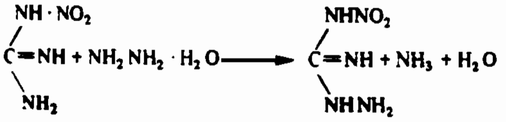

I


II

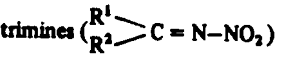
NITROAMINOGUANIDINE

Nitroaminoguanidine can be obtained by acting with hydrazine on nitroguanidine [168, 184]:


m.p. 186-187°C


(28)

By reacting with nitrous acid in acetic acid it yields 5-aminotetrazole [185]. Aminotetrazoles are related to initiating explosives obtained from aminoguanidine (Chapter XVII, and Vol. III, p. 206).



Nitrimines $\left(\begin{smallmatrix}R^1\\R^2\end{smallmatrix}\!\!>C=N-NO_2\right)$

The chemistry of nitroguanidine and the work of Büchi are related to the chemistry of nitrimines, that is, compounds containing $>C=N-NO_2$ group. The structure of this group was given by Scholl [75], but was subject to criticism and a few structures were suggested by Fusco and Trisoglio [76] and Freeman [77]. Freeman found the confirmation of the nitrimino structure by ultraviolet, infra red spectra and the transformation of the group into the primary amino group by reducing with potassium borohydride:

$$=N-NO_2 \xrightarrow{KBH_4} -NHNO_2$$

NITRODIETHANOLAMINE DINITRATE (DINA) (Vol. III, p. 36)

This interesting compound was investigated by French chemists who gave thermochemical properties: heat of combustion $-\Delta H_c = 577$ kcal/mol and heat of formation $-\Delta H_f = 70{,}5$ kcal/mol. [89].

Preparation

Desseigne [88] added some information to the method of G. F. Wright *et al.* (Vol. III, p. 36). Here are the main points of the process.

A nitrator was filled with 170 parts of acetic anhydride (99%) and 1.4 parts of hydrochloride of diethanolamine dissolved in 4 parts of acetic acid. Diethanolamine (52.5 parts) and 107 parts of nitric acid (97%) were added keeping the temperature at 10–15°C. After that mixing had been continued for 10–15 min. the product (DINA) began to precipitate. All was poured on ice (200 parts), filtered and washed with water followed by washing with hot 0.25% aqueous solution of sodium carbonate. At the end the solution should be neutralized with acetic acid. The product was finally purified by dissolving in acetone and precipitating with water containing a small amount (*ca.* 0.3%) of ammonia.

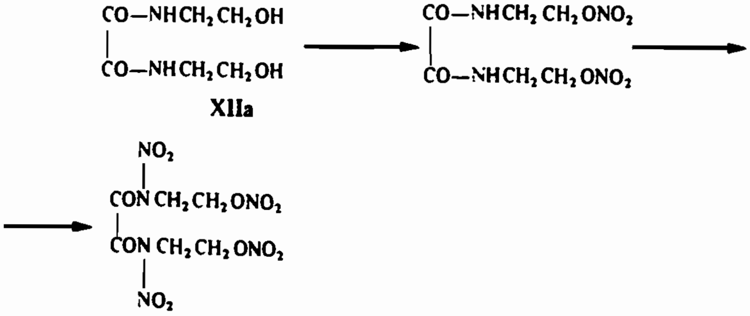
The yield was 108 parts, i.e. 90% of theoretical.
The m.p. of the product was 50.15°C.

The rate of detonation is 7730 m/s at density 1.60 and 7580 m/s at 1.55. Lead block 146% of picric acid. It shows a lower stability at 100°C and higher sensitivity to impact than tetryl [90].

Glazkova [92] in her monograph described experiments of burning DINA and the influence of various additions. The addition of dichromates of cations (particularly of potassium dichromate) increases the rate of burning.

DINITRODI-(β-HYDROXYETHYL)-OXAMIDE DINITRATE (NENO)
(Vol. III, p. 37)

Desseigne [91] repeated experiments of nitration of the amide (XIIa) in two steps:



XIIa

XIIb

(29)

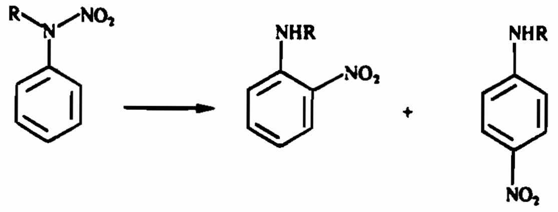
$$\begin{array}{l}CO-NHCH_2CH_2OH\\|\\CO-NHCH_2CH_2OH\end{array} \longrightarrow \begin{array}{l}CO-NHCH_2CH_2ONO_2\\|\\CO-NHCH_2CH_2ONO_2\end{array} \longrightarrow$$

$$\longrightarrow \begin{array}{l}\;\;\;NO_2\\\;\;\;\;|\\CONCH_2CH_2ONO_2\\|\\CONCH_2CH_2ONO_2\\\;\;\;\;|\\\;\;\;NO_2\end{array}$$

The nitration was difficult and required the use of nitric acid with 60% oleum at 25°C with an overall yield of 75%. Compound XIIb can dissolve nitrocellulose and could be used according to Desseigne in double base propellants.

AROMATIC NITRAMINES

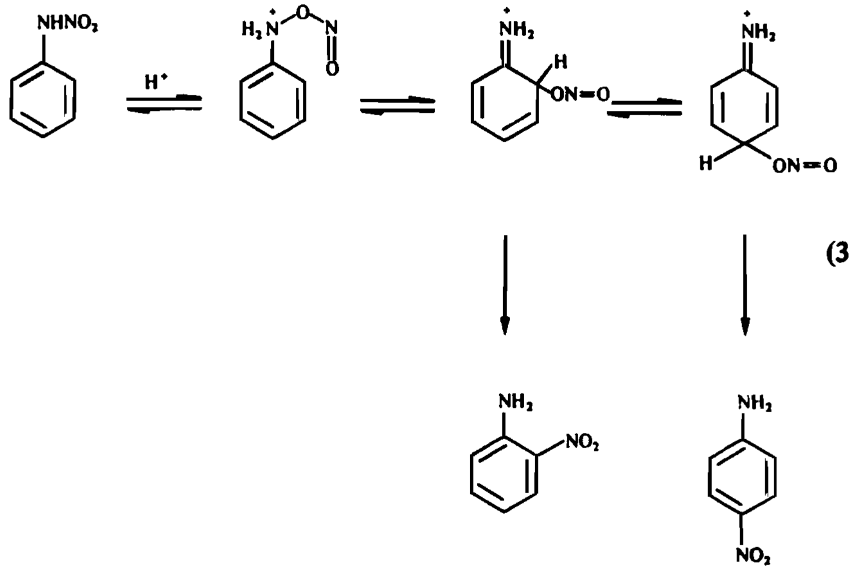
Aromatic nitramines can be subjected to 'Bamberger rearrangement' described for the first time by E. Bamberger in a number of papers since 1893 [78, 79]:



(30)

Bamberger advanced a hypothesis that the nitration of the aromatic ring of aromatic amines begins by N-nitration followed by a subsequent rearrangement. The hypothesis was examined by Holleman and co-workers [80] who concluded that ring nitration does not always proceed by way of an initial N-nitration. Also Orton with co-workers studied the mechanism of the reaction in a number of papers [81]. He concluded that the Bamberger rearrangement is an acid catalysed reaction.

Hughes and co-workers [82, 83] in a number of papers examined the mechanism of the reaction by using nitrogen isotopic [^{15}N] and [^{2}H] label. They came to the conclusion that the Bamberger rearrangement is an intramolecular mechanism. They rationalized it in terms of the formation of nitrites:



(31)

U.S. chemists [84] examined the action of 0.1 N hydrochloric acid on *N*-methyl-*N*-nitroaniline at 40°C and obtained:

ca. 52% *o*-nitro-*N*-methylaniline
31% *p*-nitro-*N*-methylaniline and
7% *N*-methylaniline.

Nitrous acid (*ca.* 13%) was also formed.

They also came to the conclusion that the rearrangement is an acid catalysed reaction.

TETRYL (Vol. III, p. 40)

In the course of the last few years the significance of tetryl has been considerably reduced. With the advent of Cyclonite (RDX) and PETN, tetryl is losing its significance and in the U.S.A. it was withdrawn from use. Also compounds similar to tetryl with *N*-methyl-*N*-nitro side group have aroused less interest lately.

Nevertheless a few published papers have appeared mainly referred to thermal decomposition of the substance. Former data (Vol. II, pp. 52–53) were confirmed in general, but completed by more detailed experiments. Thus Dubovitskii, Merzhanov and co-workers [85] examined the influence of the density of loading (m/v, where m = the mass of the substance, v = the volume) at 150°C. Some of their results are shown in Fig. 53. It can be seen that the density has little effect on the rate of decomposition. The gases evolved were composed of NO_2, NO and N_2. High (1) and low (3) density.

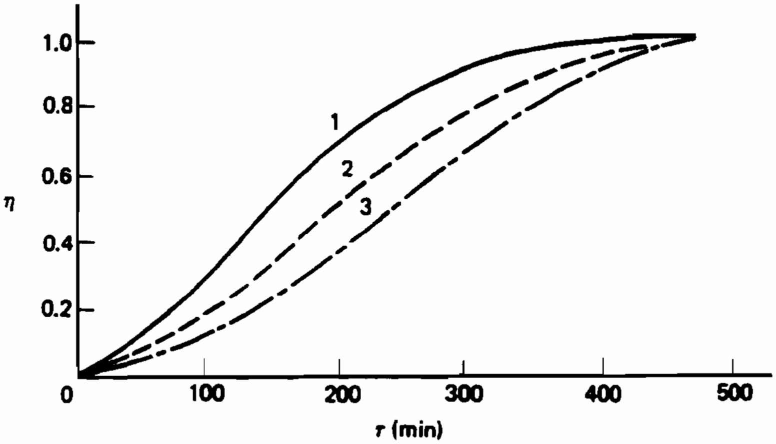


FIG. 53. Thermal decomposition of tetryl [85]. m/v in g/cm^3. 10^{-4}; 1–353.5, 2–49.4, 3–0 (removal of gases); η (degree of decomposition).

Hara, Kamei and Osada [86] obtained similar results. Among the gases from the decomposition of tetryl they also found methane. They carried out the experiments at temperatures from 150 to 175°C. By differential thermal analysis they found the endothermic (negative) peak at 131°C due to the melting of the substance and exothermic decomposition occurred at 160°C. They calculated the activation energy as being 35 kcal/mol. This is in agreement with formerly obtained results (Vol. III, p. 53).

Pre-heating of tetryl increases the rate of burning of the substance. This was already shown by Andreev (Vol. III, Fig. 6), by his later work [94] and substantiated by M. M. Jones and Jackson [87] and Japanese authors [86]. The latter authors found for example that preheating the sample to 180°C lowers its m.p. by 20°C and the decomposition temperature by 12°C. They also examined the samples of tetryl heated at 165°C for 3 hours: by liquid chromatography, by TLC, NMR and mass spectrography. They found that 2,4,6-trinitroanisol and picric acid are formed on the thermal decomposition of tetryl at 160–200°C.

Burning of tetryl is discussed in the monograph by Glazkova [92] and reference is given to the early work of Hinshelwood [93] who pointed out that thermal decomposition of tetryl produces picric acid which plays the part of a catalyst of the decomposition. The rate of burning of tetryl under pressure increases by addition of potassium bichromate, according to Glazkova [92].

Thermal decomposition of tetryl was reviewed by Dubovitskii and Korsunskii [4].

HETEROCYCLIC NITRAMINES (Vol. III, p. 77)

Cyclonite (Hexogen, RDX) (Vol. III, p. 77)

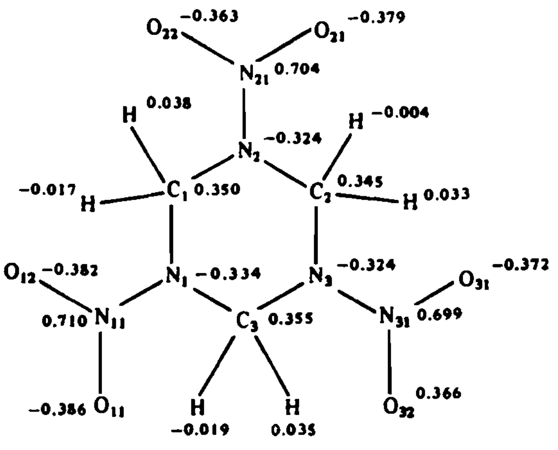
Cyclonite (RDX in Anglo-Saxon literature, that is, Research Department Explosive) 1,3,5-trinitro-1,3,5-triazacyclohexane is at present one of the most important explosives. Over the last two decades extensive literature has been dedicated mainly to its analysis and application.

Structure

The structure of RDX has been characterized by X-ray analysis [95]. Dipole moments measurements to establish stereochemistry of nitramines have been extensively used by a few authors: G. F. Wright [96], Calderbank and Pierens [97].

The latter authors [97] found that the chair calculation 22.27 D corresponded best to experimental value 19.1 D (boat conformation and twist boat conformations gave calculations 5.81 D and 7.04 D respectively). Calderbank and Pierens also measured and calculated the Kerr effect (electric birefringence) and found the calculated value for chair conformation (−2868) fitted best to the experimental figure (−2102). The boat and twist boat conformations gave figures distant from the experiments (+172 and +164 respectively). The conclusion of these authors was that the preferred conformation of cyclonite corresponds in 70% at least of chair.

Delpuech and Cherville [98] calculated electric charges in cyclonite by CNDO method [99]. The results are given in Fig. 54.



Cyclonite (Hexogen, RDX)

FIG. 54. Electron density of cyclonite [98a].

Conformation of Cyclonite was studied by the NMR technique by Stefaniak, Urbański, Witanowski and Januszewski [197].

Spectroscopy of Cyclonite

Electronic spectrum of cyclonite has been examined by a number of authors [7, 100, 101] who found a maximum at 202 nm and a shoulder at 236 nm. Later examination of spectra [102] confirmed these results for cyclonite dissolved in ethanol. In methanol they were slightly different: 204 and 234 nm.

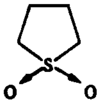
Infra-red spectroscopy was given in the monograph of Bellamy [103].

Chemical Properties

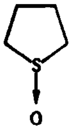
Contrary to aromatic nitro compounds cyclonite does not readily give adducts. No charge–transfer complexes are formed with amines. Selig [104] established the existence of an adduct of cyclonite with hexamethylphosphoric triamide (HMPT). Another complex with tetrahydrothiophene-1,1-dioxide (sulfolane) was described by French authors [105, 106]. Recently Selig [107] reported that a number of heterocyclics with nitrogen or sulphur could form the adducts. Relatively stable equimolar complexes were obtained with:

$O \leftarrow P[N(CH_3)_2]_3$

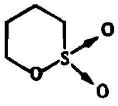
XIII



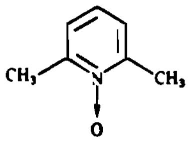
XIV



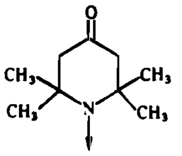
XV



XVI



XVII



XVIII

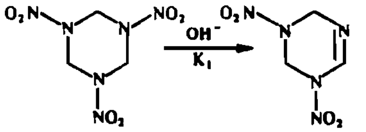
XIII – HMPT, XIV – Sulpholane, XV – Tetrahydrothiophene-1-oxide, XVI – 1,4-Butane sultone, XVII – 2,6-Litidine-N-oxide, XVIII – 2,2,6,6-Tetramethyl-4-piperidone-1-oxyd.

Compounds XIV and XVIII are 'selective' to hexogene: they do not form adducts with octogene, whereas all others form adducts with both: hexogene and octogene.

Cyclonite is decomposed in concentrated sulphuric acid and the decomposition yielded most likely nitronium ion (Vol. III, p. 81). This is evidenced by the fact that a solution of cyclonite in sulphuric acid can nitrate aromatic compounds.

Thus Holstead and Lamberton [108] obtained *p*-nitroacetanilide with a 45% yield when acting on acetanilide with a solution of cyclonite in 95% sulphuric acid. T. Urbański and Zyłowski [65] nitrated anthraquinone with the same solution at room temperature for 24 hours. The yield of 1,5-dinitroanthraquinone was 36%.

Croce and Okamoto [109] described a cationic micellar catalysis (Chapter IV) of aqueous alkaline hydrolysis of cyclonite (and octogene). Denitration occurred in the presence of ethylhexadecyldimethylammonium bromide. Liquid chromatography was used as the analytical method (32):



(32)

1,3,5-Triaza-3,5-dinitrocyclohexene-1-ene resulted.

Thermal Decomposition

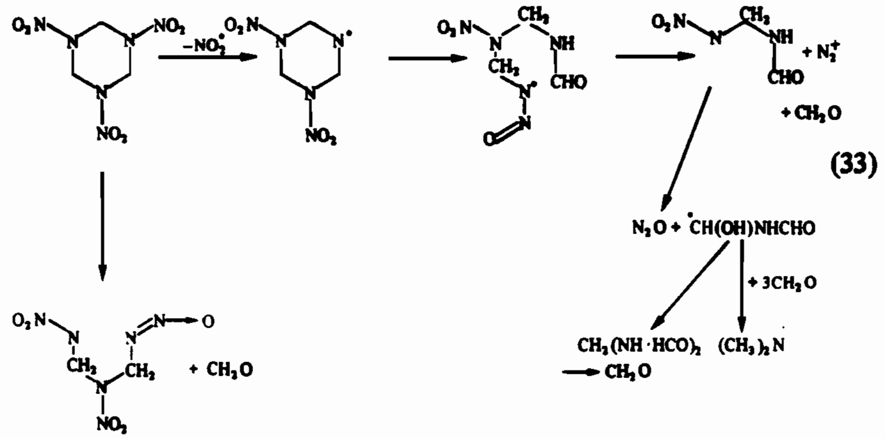
Thermal decomposition of cyclonite was investigated by numerous authors (also Vol. III, p. 83): [110–115]. Maksimov [111] described several experiments of decomposition of cyclonite and octogene as solid substances and in solution. The energy of activation was calculated as $E = 52.0$ kcal/mol. $\log_{10} B = 19.1$.

Figure 55 shows the decomposition of cyclonite in solution in *m*-dinitrobenzene at 160–200°C. A concentration of 4% was used with the exception of the sample examined at 190°C where the concentration was 13%. The energy of activation was $E = 39.7$ kcal/mol, $\log_{10} B = 14.3$. One of the conclusions of the authors was that cyclonite decomposes faster in solution than as a solid. This is in an agreement with existing views that explosives in a liquid form decompose faster than solid due to the transition of the solid to a higher energy liquid state (experiments by T. Urbański *et al.*, Vol. II, pp. 181–183). According to Maksimov the decomposition of hexogene at 180°C in solution is 16 times faster than in the solid state.

Cosgrave and Owen [115] and Debenham and Owen [170] studied the decomposition of cyclonite at 195°C and 173–184°C respectively. They came to the conclusion that the initial decomposition takes place in the vapour phase and is followed by a more rapid decomposition in the liquid phase (e.g. a solution of cyclonite in 1,3,5-trinitrobenzene [170]).

Major products were: hydroxymethyl formamide and its polymers. The following is a list of products of the decomposition: N_2, N_2O, NO, CO_2, CO, CH_2O, H_2, H_2O, HCN, HCOOH, NH_3, NO_3^-, NO_2^- and the polymer mentioned above.

They gave a simplified presentation of the thermal decomposition of hexogene (33):



(33)

Other work on thermal decomposition of cyclonite was done by Wilby [171], Rosen and Dacons [172], Rauch and Fanelli [173] and Batten [174].

Recently Kishore and Laye [116] examined thermal decomposition of cyclonite by differential scanning calorimetry. The curves of the decomposition are of an 'S' shape (similar to those of tetryl – Fig. 53). Isothermal curves are similar to Figs 55 and 56. The author calculated the *E* value of decomposition of cyclonite in an open vessel as being 41 ± 2 kcal/mol. They also reported the values of *E* obtained by other authors. In addition to those given in Vol. III, p. 83 (by Robertson), they are those of:

Rogers and Morris [117] 67.5 kcal/mol
Adams [118] 45.5 kcal/mol (203.5–261°C)
Batten and Murdie [119] 67.0 kcal/mol (179–200°C)
Hall [120] 45.2 kcal/mol (210–261°C).

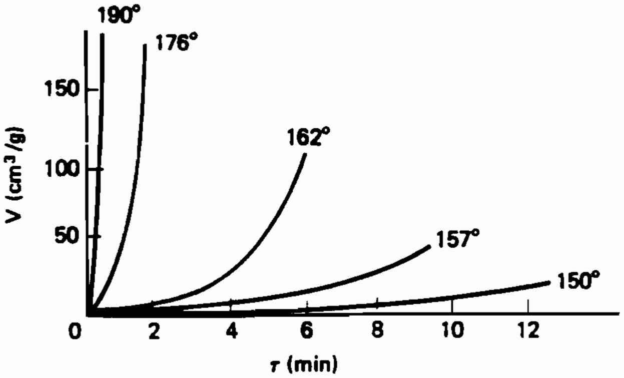


FIG. 55. Thermal decomposition of solid cyclonite [111].

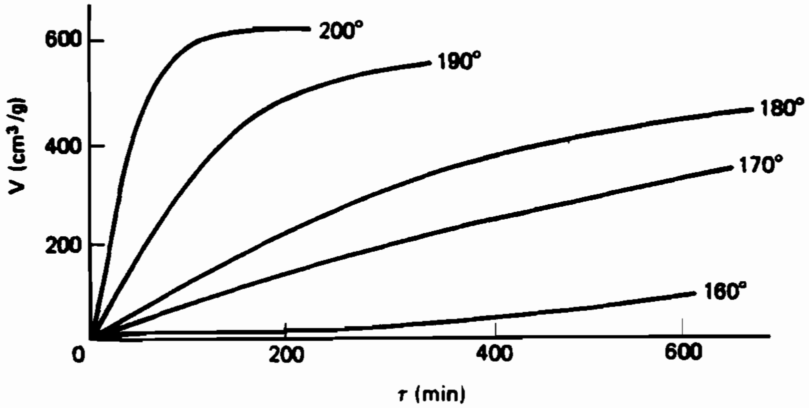


FIG. 56. Thermal decomposition of cyclonite in solution [111].

Kishore concluded that the figure closest to 45 kcal/mol was the most reliable. The order of the reaction is 0.6 according to the same author. See also the review article of Dubovitskii and Korsunskii [4].

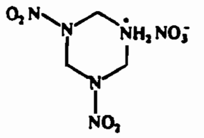
Preparation of Cyclonite (Vol. III, p. 87)

Nitration of hexamine. Very little can be added to the mechanism of the reactions leading to cyclonite, as given in Vol. III.

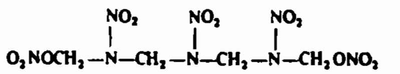
With regard to the nitration of hexamine with nitric acid Singh [121] brought a small change to the charge distribution in compound (VIb – Vol. III, p. 89), and Lamberton *et al.* [122] added some more information on compound XIX (the same as Ia, Vol. III, p. 91).

Bell and Dunstan [123] subjected reactions of hexamethylenetetramine with nitric acid, at various temperatures, to a detailed examination. Addition of water to nitrolysis solution obtained by the action of nitric acid (98%) on hexamine at –30°C yielded P.C.X., that is 3,5-dinitro-3,5-diaza-1-azoniacyclohexane or 3,5-dinitro-3,5-diazapiperidinium nitrate (XIX) (Vol. III, p. 91, Ia). The nitrolysis mixture kept at 0°C for 2 hours yielded 83% RDX and traces of the linear compound: derivative of tetra-azanonane (IX of p. 89, 91, Vol. III).

Acetic anhydride reacted with hexamine by nitrolysis to yield RDX, and linear derivatives of 2,4,6-trinitro-2,4,6-triazaheptane: diacetoxy compound (Vol. III, p. 91, XV and dinitroxy (XX):

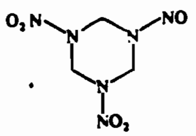


XIX



$$O_2NOCH_2-\underset{|}{\overset{NO_2}{N}}-CH_2-\overset{NO_2}{N}-CH_2-\overset{NO_2}{N}-CH_2ONO_2$$

XX



XXI

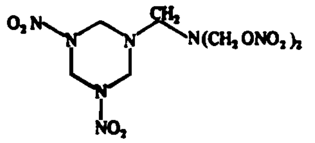
A small quantity of linear dinitroxytetra-azanonan (IX, Vol. III, pp. 89, 91) was also formed.

By adding aqueous sodium nitrite to the nitrolysis mixture at –30°C, 75% yield of 1,3-dinitro-5-nitroso-1,3,5-triazacyclohexane (XXI) was obtained.

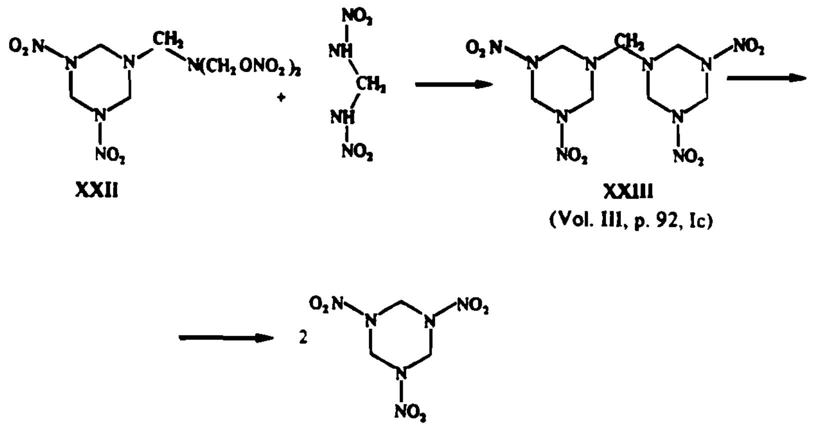
An interesting reaction was found when cold (–30°C) nitrolysis mixture was treated with methylenedinitramine $CH_2(ONO_2)_2$ and after that kept at 30°C for 15 min. The yield of RDX was almost doubled – from 82 to 145% calculated on the basis of hexamine ⟶ one mole of RDX.

Larger ring nitramines – homologues of RDX – were obtained by adding dinitramines such as ethylene and trimethylenedinitramine. Homologues of RDX with cycloheptane and cyclooctane ring resulted.

These experiments suggested that bis(nitroxymethyl)aminomethyl intermediate (XIII, Vol. III, p. 91) can be a probable precursor which upon nitrating to dinitrate and reacting with methylenedinitramine eventually yielded RDX according to scheme (34).



XXII (Vol. III, p. 91, XIII)



(34)

Preparation of Cyclonite from Hexamine Dinitrate Acetic Anhydride

The methods by W. E. Bachmann (in the U.S.A.) and Köffler (in Germany) – Vol. III, p. 111 have now received particular attention in view of the fact that the route with acetic anhydride can lead to the formation of Octogene (HMX).

Reed [124] described the reaction of hexamine, nitric acid, trifluoroacetic anhydride in the presence of liquid SO_2 which is a very good solvent for hexamine. The reaction yielded (85%) 1-trifluoroacetyl-3,5-dinitro-1,3,5-triazacyclohexane, m.p. 131–132°C.

Explosive Properties of Cyclonite (Vol. III, p. 84)

Little can be added to the information given in Vol. III as regards explosive properties of Cyclonite. Interesting information was recently given by Institut Franco-Allemand de Recherches de Saint-Louis, France [186]. The rate of detonation of single crystals of cyclonite was found to be different along different crystal axis:

(001)	8700 m/s
(110)	8587 m/s
(111)	8437 m/s

T. Urbański and Galas [187, 188] examined the influence of non-explosive liquids on the velocity of detonation of cyclonite. The results with two liquids: water and glycerol are collected in Table 62. The shape of the curve: velocity of detonation against the proportion of liquids is much the same as for PETN and liquids as depicted in Fig. 42.

TABLE 62. Detonation of cyclonite with water and glycerol [187, 188] in steel tubes 20/26 mm diameter, detonator No. 8 with 10 g PETN

Proportion of liquid %	Density		Rate of detonation m/s		Difference V_0-V_r
	Total ρ	Real ρr	Observed V_0	at density ρr V_r	
Water					
0	1.45	1.45	7705	7705	0
10	1.45	1.31	7235	7280	−45
20	1.45	1.16	7775	6820	935
30	1.45	1.02	7070	6365	705
Glycerol					
10	1.40	1.26	7360	7125	235
20	1.40	1.12	7505	6685	820
30	1.40	0.98	7875	5240	1635
35	1.40	0.91	7740	6015	1725
40	1.40	0.84	7555	5790	1765

Apin and Velina [189] also examined the velocity of detonation and the pressure of detonation of explosives with water. Apin, Pepekin *et al.* [190] subjected the cyclonite–water system to a detailed thermochemical examination.

They found a straight line increase of the heat of detonation against water content from 0 to 24% of water: 1380 cal/g of dry substance and 1187 cal/g of a mixture of 76% cyclonite and 24% water. This gives a calculated value for the dry substance 1565 cal/g. It corresponds also to the maximum of the increase of the velocity of the detonation V_0-V_r (Table 62) [187, 188]. Further addition of water (above 24%) does not increase the heat of detonation [190] and the increase of the velocity of detonation V_0-V_r drops [187, 188].

Apin, Pepekin *et al.* [190] explain the phenomenon of the increase in the rate of detonation by adding water in the following way. The liquid plays the part of a confinement which prevents the dispersion of the products of detonation and prolongs the time necessary to complete the reaction in a similar way to the action of a confinement. This is certainly true but according to T. Urbański [187–188] the importance of the covolume [191] should also be taken into consideration. Another factor which should be considered is the increase of entropy (S) and Gibbs free energy (G = H–TS) which is higher in a mixture than in the individual ingredients and T. Urbański [192] advanced an hypothesis that the high entropy and free energy play an important part in properties of explosives such as their rate of detonation and sensitivity to impact. According to T. Urbański the high entropy and free energy of mixtures is one of the factors which increases the rate of detonation of a solid explosive by adding a non-explosive liquid.

Manufacture of Cyclonite (RDX) according to Mario Biazzi S.A. (Vevey) [125]

This process consists of continuous nitration of hexamine with nitric acid (98.5%), continuous 'decomposition' of the secondary products formed during nitration and continuous filtration of RDX from its spent acid.

The hexamine, dried and sifted is fed into the first nitrator with a constant feeding rate. The nitric acid is fed from a constant level overhead tank. The feeding rate is regulated by the remote control of a pneumatic valve. The contents of the first nitrator continuously overflow into the second and then to the third (last) nitrator.

From the last nitrator all overflows to the decomposing vessels. Decomposition is initiated by filling the first decomposer with some of the nitric acid (50%) obtained from the absorption of the nitrous gases evolved during decomposition. The RDX crystallizes out and is continuously separated by vacuum filters. The RDX cake is flushed on the filter with cold water. The dilute nitric acid goes through the filter into an intermediate vacuum tank equipped with a strainer retaining all the RDX which may escape from the filter. From the tank the acid is pumped into storage. The acid washing water is collected in a separate tank from where it is evacuated by pumping.

The RDX cake washed from the filter cloth is continuously evacuated into a slurrying tank where it is mixed with water and transferred by means of water injector to another building. Reactors are cooled with Freon 12.

During nitration gases are evolved. They are drawn from the equipment vessels by means of a fan to a tower where they are met with water in a counter-current.

The acid RDX/water slurry flows into a continuous vacuum filter, the transport water is drawn through the filter into an intermediate tank with a strainer to retain traces of RDX. From the filter RDX falls into a suspension funnel with aqueous sodium bicarbonate. The suspension flows into the stabilization battery made of a series of steam injectors separated by cooling elements. The injector stabilization battery removes the occluded acid. The injection of steam reduces the size of crystals and removes the acid.

From the stabilization battery, the RDX/water mixture flows to the phlegmatizer or to a continuous filter. If RDX is phlegmatized, this is done in three jacketed and stirred vessels where crystals are coated with wax. The molten wax is added to the first phlegmatizer and is hardened by cooling in the second and third vessels and finally filtered. Moisture content (both unphlegmatized and phlegmatized) – 10%.

Specification for Hexamine 'Nitration Grade'
Moisture max. 0.2%
Crystal size: over 500 μ max. 30%
300–500 μ 70–85%
less than 200 μ max. 10%
Dust, sulphates, chlorides, heavy metals – absent
Water insoluble max. 0.10%
Ash max. 0.03%

Consumption for 1000 kg RDX
Hexamine 866 kg
Nitric Acid (calculated as 100%) 8530 kg
Process water 21000 kg

Phlegmatizing agent – according to requirements (see below)
Neutralizing agent ($NaHCO_3$) 3–5 kg.

Steam 4500 kg
Electric energy 1440 kWh
Compressed air 100 Nm^3

Specification for RDX is according to U.S. Standards for type A product.

Specification for Cyclonite (Hexogen)

According to the Encyclopedia of Fedoroff and Sheffield [126] the specifications for Cyclonite in Germany and in the U.S.A. are as follows.

Germany (Vol. III, p. 105). Hexogen should be crystalline, dry, colourless and screened. Hexogen intended for use in detonators and percussion caps should be purified by crystallization (e.g. from nitrobenzene). Hexogen intended for phlegmatization and used in boosters should contain water.

Melting point: (a) for W-, K- and SH-Salz (Vol. III, p. 104) m.p. should be above 200°C, (b) for E-Salz above 190°C.

Granulation. For boosters hexogen should pass through a 0.75 mm sieve (DIN 8), for ignition charges through a 0.60 mm sieve (DIN 10).

Loss of Weight: should not exceed 0.1% of 10 g sample for 5 hr at 100°C. Sulphate and Chlorine should be absent.

pH should be below 7.5. Formaldehyde – only trace. Acidity: 10 g sample should not use N/20 NaOH more than 3.0 cm^3 for E-Salz, 2.0 cm^3 for SH- and K-Salz, 0.3 cm^3 for recrystallized W- and K-Salz and any other kind of Hexogen for detonators and percussion caps.

Aceton insoluble – max. 0.1%. 120°C KI test – no discoloration after 10 min and only slight discoloration after 20 min.

U.S.A. Specification of 1963 covers two types of RDX and light classes based on uses and granulation.

Type A – made by the nitric acid method,
Type B – made by the acetic anhydride process.

Properties:	Type A	Type B
m.p.	200°C	190°C
Aceton insoluble max.	0.05	0.05
Inorganic insoluble max.	0.03	0.03
Particles retained on US Std. Sieve No. 60 max.	5	5 particles
Acidity max.	0.05% as HNO_3	max. 0.02% as CH_3COOH.

For the use of various classes of the fineness – see Encyclopedia [126].

Disposal of Waste Cyclonite [126]

A five per cent solution of NaOH should be brought to boiling point by injecting steam. Cyclonite should be added in small portions. After adding all the cyclonite boiling should be continued to be discharged into a sump.

Toxic Properties of Cyclonite (Vol. III, p. 86)

More information was collected on toxicity of Cyclonite. Experiments with animals confirmed earlier findings of convulsions caused by Cyclonite. The important observations on humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident has been recorded [195].

EXPLOSIVES WITH CYCLONITE AS A MAIN COMPONENT

The *Encyclopedia of Explosives* [169] classifies the explosives with cyclonite into three groups: A, B and C.

Group A consists of cyclonite desensitized with waxes, this was originally used during World War II. In Great Britain cyclonite was desensitized with 9% beeswax. In Germany Montan was used (Vol. III, pp. 105, 113) in quantity 5–10%. In the U.S. synthetic waxes are used: compositions A3 and A4 are composed of 91% RDX/9% wax and 97% RDX/3% wax respectively. The composition A3 was made by heating a water slurry of RDX to 100°C and adding the wax with a wetting agent. After the wax melted, all was cooled, filtered and dried at 75°C. Composition A5 contained 1.0–1.5 stearic acid (Type I) or 1.6% stearic acid and 0.4% graphite (Type II).

Aluminized composition A of 92% RDX and 8% aluminium was originally intended for an armour piercing shell, but was found to be too sensitive to shock.

Group B are castable mixtures of RDX, TNT and some of them were known as Cyclitols. Various proportions of RDX and TNT were used, for example in Germany during World War II: Cyclitols 50/50, 53/47 for bombs and demolition charges, cyclitol 60/40 for some shells, cyclitol 20/80 containing 20% cyclonite, 80% TNT and the addition of 1% Montan wax.

The U.S.A. used mixture cyclonite/TNT in proportion 60/40 with 1% of synthetic wax added (composition B) or without wax (composition B-2). Other compositions of cyclonite/TNT were: 75/25, 70/30 and 65/35. The rates of detonation varied from 7840 m/s (composition B) to 8060 m/s (composition 70/30), the densities were: 1.68–1.71.

Group C are plastic explosives (Plastic explosives in Great Britain, Explosifs plastiques in France, Plastit in Germany).

U.S. Composition C contained after several modifications, such as Composition C-3: cyclonite 77%, DNT 10%, MNT 5%, TNT 4%, Tetryl 3% and Nitrocellulose 1%. The last five ingredients served as a plasticizer. It gave lead block test 117% of TNT. It could withstand being plastic between −29° and +77°C.

Composition C-4 developed by Ottoson and Lerner (according to [169]) contains 91% cyclonite and 9% of the plasticizer composed of 5.3% di-(2-ethylhexyl) sebacate, 2.1% polyisobutylene and 1.6% motor oil. It remains plastic between −57° +77°C.

A considerable number of explosives existed in different countries during World War II. Most of them contained Cyclonite, TNT and aluminium with desensitizing waxes. Their compositions are given in the Encyclopedia [175]. An interesting substitute for TNT in Germany was a castable explosive composed of 50% methylamine nitrate, 35% sodium nitrate, 15% Cyclonite. A German Füllpulver Nr 86 consisted of ethylenediamine dinitrate 46%, RDX 18% and wax 36%. German plastic explosives contained liquid or semi-liquid nitroaromatics with nitrocellulose.

OCTOGEN (HMX) (Vol. III, p. 117)

There is a growing interest in Octogen (HMX in Anglo-Saxon literature, High-

Melting-Explosive), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane. This is due to remarkable explosive properties manifested by a very high velocity of detonation – over 9000 m/s (see explosive properties, p. 390). Also in some countries it is regarded as a heat resistant explosive because of its high melting point – 276–280°C d (Chapter VII).

The fact that a monograph has recently appeared [5], indicates the great interest being shown in Octogen.

Structure and Physical Properties

Octogen exists in four polymorphic modifications: I–IV or α, β, γ, δ which are most likely conformational modifications. Each of the four can be obtained by crystallization from a different solvent keeping a different rate of cooling of the solution.

TABLE 63. (see also Table 21, Vol. III, p. 118)
Some properties of octogen modifications*

	β	α	γ	δ
Region of stability	room temperature to 115°C	115–156°C	156°C	156-m.p.
Melting points (on rapid heating)	246–247°C	256–257°C	278–280°C	280–281.5°C
Molar refraction				
R calculated	56.1	55.7	55.4	55.9
58.0				
Sensitiveness to impact				
mass in kg/height	5/15	1/20	1/20	1/10
energy of impact kg/cm^2	0.75	0.2	2.2	0.1

* Compiled from [5].

Here is the description according to Fedoroff and Sheffield [127]:

The common modification, stable at room temperature β-HMX is obtained by very slow cooling of HMX dissolved in acetic acid, acetone, cyclohexanone, acelonitrile, nitric acid or nitromethane. The crystals are monoclinic.

α-HMX can be formed from the same solution as above under condition of rapid cooling. The crystals are orthorhombic.

γ-HMX are also formed from the same solution but under a very rapid cooling. The crystals are monoclinic.

δ-HMX are formed from solvents in which the substance is only slightly soluble, such as acetic acid in small amounts and by rapid cooling by pouring over ice. Selig [128] obtained δ modification by crystallizing β from *N,N*-dimethyl-*p*-toluidine. The crystals belong to hexagonal system.

As regards to crystal shape and more information on crystallographic systems – see [5].

The change of modifications at different temperatures and their relative stability is given in Fig. 57 based on the literature [129, 130].

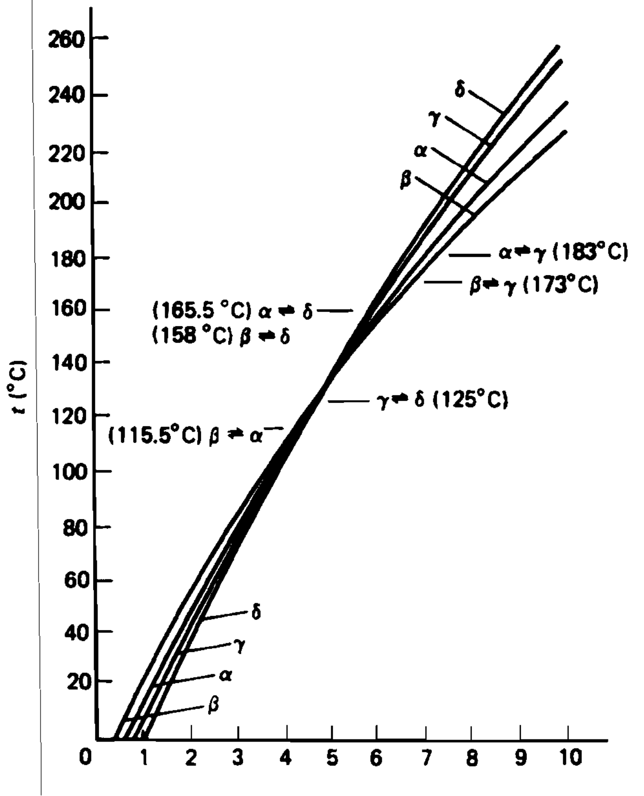


FIG. 57. Transition of octogen modifications [128, 129].

On the abscissae is given a relative value of free energy. The most stable modifications of octogene are above the point of crossing the curves.

X-ray and ESR analysis of β-octogen gave the structure presented in Fig. 58 according to Cady, Larsen and Cromer [131].

They found that the nitro groups in octogen are in both equatorial and axial positions. The presence of axial groups was explained by Stals [133] as being due to mutual electrostatic actions of nitramino groups. The conformation of α, β and γ-octogen based on dipole moments measurement was given by G. F. Wright [96] and depicted in Fig. 59.

Charge distribution in β-octogen [98a] is presented in Fig. 60.

According to data given in the monograph by Orlova *et al.* [5] the following were enthalpies – ΔH of the change of modifications:

	temperatures t°C	– ΔH cal/g
α → δ	193–201	5.97 ± 0.18
β → δ	167–183	7.91 ± 0.11
γ → δ	175–182	2.25 ± 0.08

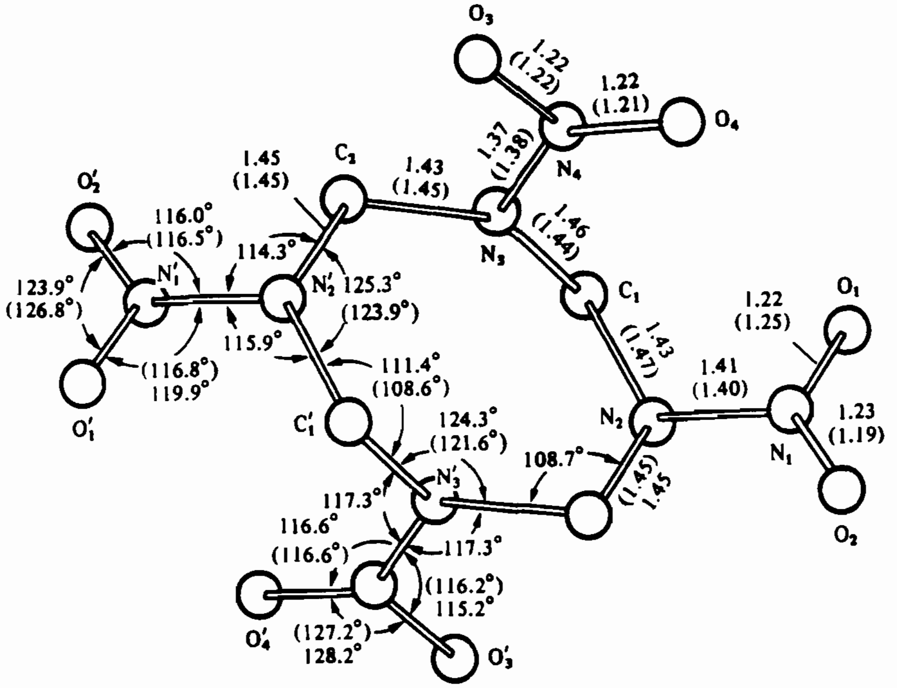


FIG. 58. Structure of β-octogen [130, 131]. Data from ESR are given in brackets.

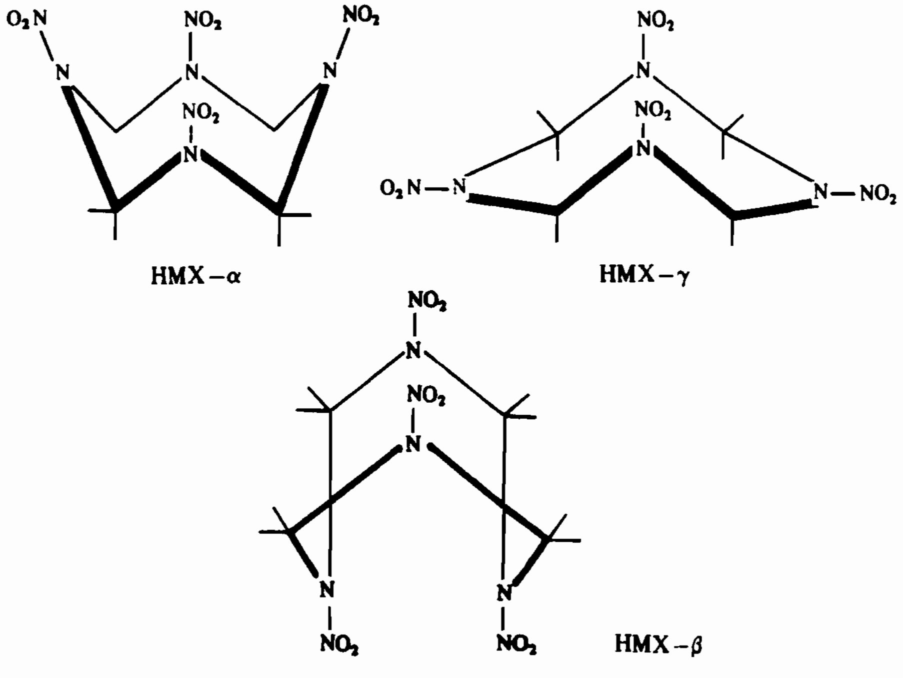
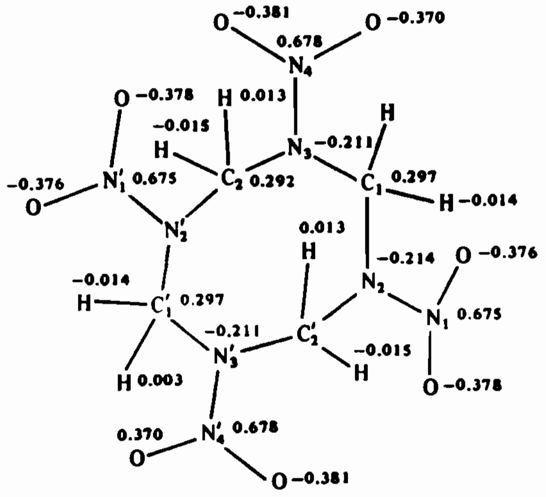
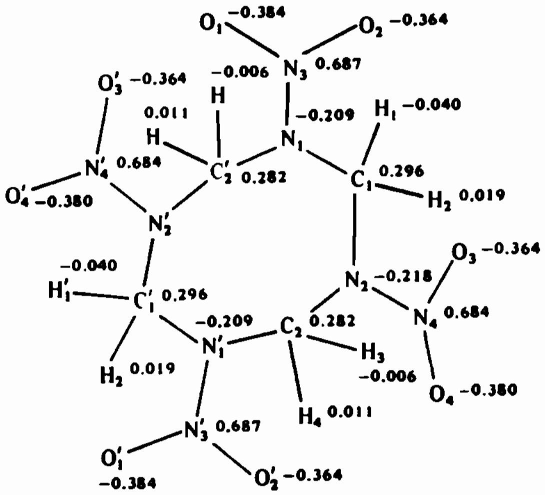


FIG. 59. Conformation of α-, β- and γ-octogen [96].



Octogen, HMX – β



Octogen, HMX – α

FIG. 60. Charge distribution in octogen (α- and β-), according to Delpuech and Cherville [98a].

Ultraviolet spectra of octogen were examined by a number of authors [134, 135, 102]. All of them found two maxima in ethanol: 201 and 206 nm.

Infra red spectra were also examined and gave clear differences between crystalline modifications [95, 96, 136]. According to G. F. Wright [96] this could serve as an analytical tool for distinguishing the modifications when crystalline was solid. Raman spectra were taken for β-HMX and isotopes: ^{15}–NO$_2$, ^{15}–N–NO$_2$, ^{13}–C and d$_8$ HMX [137]. One of the conclusions was the presence of hydrogen bonds between NO$_2$ and CH$_2$ groups.

Volk and Schubert [138] described mass-spectrography and Lamberton and co-workers [139] NMR spectroscopy of HMX and other nitramines.

Solubility of Octogen

According to the *Encyclopedia of Explosives* [127] the solubility of octogen is as follows in grams of HMX, in 100 g of the solution, at 25°C:

In acetic acid	0.0375 g
acetone	0.96
acetonitrile	1.98
cyclohexanone	2.11
dimethylformamide	4.4
ethyl acetate	0.02

In 1,2-dichloroethane: 0.02 at 24°C and 0.125 at 70°C.

In general, octogen is less soluble than cyclonite (Vol. III, pp. 79–80).

Specific heat of octogen at –75°C in 0.153 cal/g/°C,

0	0.228
25	0.248
50	0.266
75	0.288
100	0.295

The figures are taken from the Encyclopedia [127].

Chemical Properties

One of the characteristic features of octogen which distinguishes that compound from hexogen is that octogen readily forms additional complexes – probably charge–transfer complexes. They have been described by a number of authors [140, 136] but mainly by Selig [141]. He described complexes of octogen in molecular ratio 1:1 with amines, for example

aniline	m.p. 172°C

o-, *m*- and *p*-toluidine, m.ps 166°, 134° and 139°C respectively 1- and 2-naphthylemine; m.ps 203° and 148°C respectively, with some substituted phenols:

o-cresol	m.p. 108°C
1-naphthol	m.p. 182°C

With some compounds, for example *N*-methyl-2-pyridon, *N*-methyl-*p*-toluidine, *o*-nitroaniline, hexamethylphosphotriamide the molecular ratio octogen: second compound is 2:1.

The X-ray analysis of octogen showed a 'sandwich' structure very common in CT-complexes.

The difference between hexogen and octogen as regards the formation of complexes can be used for the separation of octogen from hexogen.

Enthalpy of decomposition of complexes on melting is of the order of 2–3 kcal/mol.

Octogen did not decompose when boiled with 2% nitric and sulphuric acid, but concentrated sulphuric acid decomposed in a way similar to the decomposition of hexogen but slower than that of the latter [142]. Ion NO_2^+ is probably present in the octogen–sulphuric acid solution.

On the other hand, octogen is more reactive with alkali than hexogen. A solution of 1% Na_2CO_3 decomposed octogen completely after prolonged boiling. A solution of sodium carbonate or sodium hydroxide can be used to decompose the residual octogen. The irradiation of octogen with ultraviolet light [154] liberated stable free radicals $\cdot NO_2$.

Thermal Decomposition

Octogen is probably more stable than Cyclonite and is comparable with TNT at 150°C in the vacuum stability test [127].

A scanning calorimeter can give information on the decomposition of various forms of octogen in the temperature range 180–210°C [13]. Maksimov [111] examined the behaviour of octogen at high temperatures. The decomposition of solid samples at temperatures from 183° to 230°C was measured by determining the volume of gaseous products, some of the curves are given in Fig. 61. The energy of activation was calculated: 37.9 kcal/mol and $\log_{10} B = 11.2$. The decomposition of a 2% solution in *m*-dinitrobenzene was examined at temperatures [171] up to 215°C. Some of the curves are presented in Fig. 62. The energy of activation was found to be $E = 44.9$ kcal/mol and $\log_{10} B = 16.0$. In solution the decomposition was faster than that of the solid substance. Octogen is decomposed much slower than hexogen, in other words exhibits much better stability than hexogen.

The problem of octogen stability was tackled in similar ways by a number of authors: Baum and Shipitsin [143], Maycock *et al.* [144, 145], Rogers and Morris [146], Hall [147], Kimura and Kubota [148].

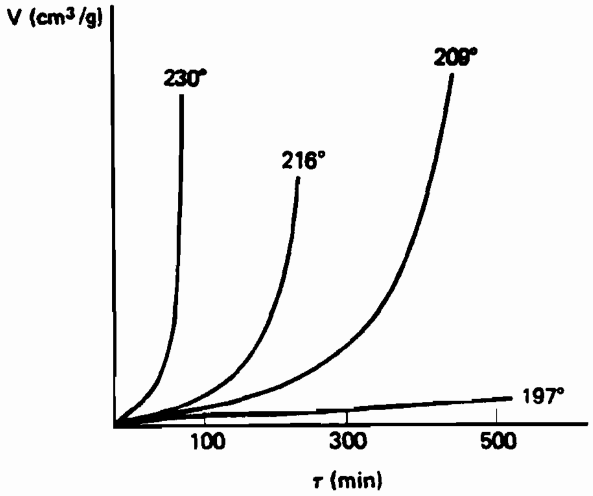


FIG. 61. Thermal decomposition of solid octogen [111].

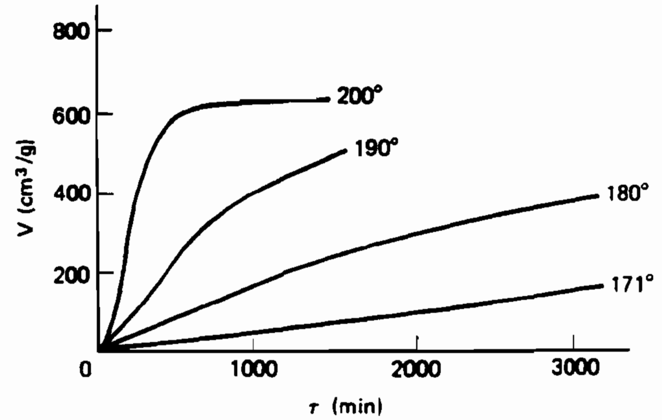


FIG. 62. Thermal decomposition of octogen in solution [111].

The induction period on a heated surface for octogen was found to be [149]:

at	350°	300°	280°	275°C
	1.7	5.3	10.0	12.3

The statement by Henkin and McGill [150] is interesting in that octogen, placed on a copper surface of 360°C, does not decompose. There is no doubt that octogen is a heat resistant explosive.

Robertson [151] and Suryanarayana and co-workers [152] have reported that formaldehyde is one of the major products of the decomposition of HMX. Suryanarayanan *et al.* concluded from studies on isotopically labelled HMS that the thermal degradation of HMX is mainly accompanied by C–N rather than N–N rupture. Amongst other decomposition products, hydroxymethyl formamide was found [153]. When kept at a temperature of 200°C β-form passes into a less stable δ-form. This explains an interesting fact described by Haeuseler [167] that is, β-octogen in a hermetic container exploded after being kept for 30 min at 200°C.

It should be pointed out that the behaviour of octogen at high temperature offers some other less expected features. Thus the very high figures of the activation energy of α- and β-octogen were found to be of the order of 150–230 kcal/mol for the decomposition temperatures from *ca.* 190°C to m.p. (*ca.* 280°C) [146–148].

Kimura and Kubota [148] tried to find a tentative explanation for such high figures in terms of autocatalytic reactions. See also the review of Dubovitskii and Korsunskii [4].

Thermochemical and Explosive Properties

The following data were given in [5] and [127]:

Heat of explosion of octogen is 1356 kcal/kg (water–liquid)
and 1222 kcal/kg (water–gas)
Heat of combustion 2255–2362 kcal/kg, 667.4 kcal/mol
Enthalpy of formation $-\Delta H_f = 17.93$ kcal/mol
(or 25.0 kcal/mol).

The strength of the explosive in ballistic mortar and in lead block was: 150% and 145% respectively, velocity of detonation 9124 m/s at the density 1.84. The detonation pressure determined by the depth of the impression in a steel plate [155] was found 0.397 mm, that is 150% of that of TNT.

The rate of burning of octogen [156] depends on the pressure, but is independent of the density:

Pressure	12.5	52.0	154.0	205.0 kg/cm^2
Rate of burning				
at $\rho = 1.66$	0.489	1.48	3.91	5.20 g/cm^{2}s
$\rho = 1.02$	0.480	1.43	3.31	5.13 g/cm^{2}s

Burning can pass to the explosion. This was studied extensively by Andreev and Gorbunov [157]. Octogen of the density 0.85 and 0.93 can explode after 0.06 and 0.54 s respectively. At a density 0.94 no explosion occurred. The authors introduced the term a 'critical density' which forms a threshold of the possible passing burning to explosion.

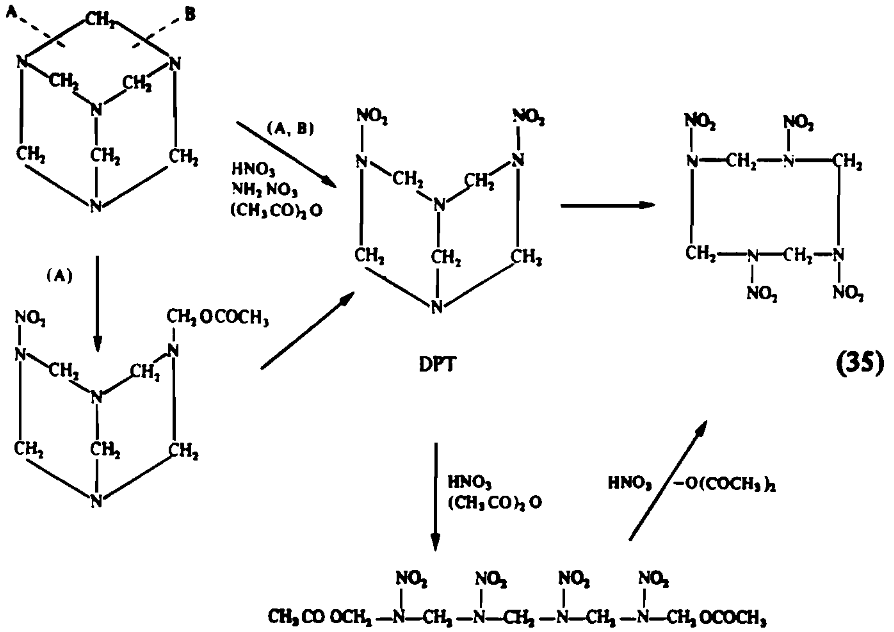
The problem of burning HMX seems to gain some importance as HMX became a common component of propellants. Particularly important is HMX with aluminium described below (p. 394).

Preparation of Octogen

Octogen (HMX) is formed in the nitration of hexamethylenetetramine ('hexamine') and is a by-product of production of cyclonite (RDX) as it was pointed out in Vol. III, p. 90. However, the statement given in Vol. III needs to be corrected. On the basis of our present knowledge, octogen which accompanies cyclonite does not reduce the power of cyclonite. On the contrary, owing to a higher velocity of detonation octogen can increase the strength of cyclonite.

W. E. Bachmann and Sheehan [158] developed a method of preparing RDX containing a small quantity of HMX. The method involved nitrolysis of hexamine with ammonium nitrate–nitric acid solution and acetic anhydride. By varying parameters of temperature and acid concentration, ammonium nitrate and acetic anhydride it was shown that the ratio RDX/HMX can be altered. These results led Bachmann and co-workers to prepare mixture rich in HMX. The optimum yield obtained was 82% conversion of hexamine to HMX/RDX mixture containing up to 73% HMX.

The mechanism of the formation of octogen can be presented by scheme (35):



(35)

Low acidity and the presence of NH_4NO_3 (and paraformaldehyde – [162]) favours the formation of octogen. Without ammonium nitrate the linear compound was formed. Higher acidity helps to obtain RDX [159].

Bell and Dunstan [162] nitrated DPT at –20°C. After warming the solution to 30°C HMX resulted in a low yield.

By using $^{15}NH_4NO_3$ W. E. Bachmann and co-workers [159] established that only 15% of nitrogen from NH_4 enters octogen, and much more (*ca.* 37%) enters hexogen. Castorina and co-workers [160, 161] used C labelled hexamine, DPT and paraformaldehyde, and found that all these compounds contribute to the formation of octogen. They obtained HMX with 15% of RDX. They isolated pure HMX by dissolving all in acetone, evaporating to form a precipitate and cooling to 25°C. The crystalline solid is HMX. The presence of RDX in the substance can be detected by acting with sodium nitroso ferricyanide on the acetone solution. A blue colour reveals the presence of RDX (reaction of S. B. Wright according to [161]).

It has been found by Picard [162] that the addition of paraformaldehyde to the mixture of ammonium nitrate–nitric acid–acetic acid–acetic anhydride increases the yield of octogen.

The following is the method described by Fedoroff and Sheffield [127] as apparently used in U.S.A.

To a 6–10 l. flask equipped with a stirrer and three dropping funnels add 785 g acetic acid, 13 g acetic anhydride and 17 g of paraformaldehyde keeping the temperature at 44 ± 1°C. Add over 15 min a solution of 101 g of hexamine in 165 g acetic acid, 320 g of acetic anhydride and 180 g of ammonium nitrate–nitric acid solution prepared by dissolving 840 g of ammonium nitrate in 900 g of nitric acid (99% concentration). The hexamine and nitric acid are added continuously in correct proportions. The mixture is stirred for 15 min. After that are added: 320 g of acetic anhydride and 271 g of nitric acid–ammonium nitrate solution in that proportion and then 160 g of acetic anhydride are added in bulk. The mixture is stirred for 60 min., 350 g of hot water are added and refluxed for 30 min. The content is cooled to 20°C by adding ice, the precipitate is collected and washed with three portions of cold water.

The yield of β-HMX is 95% of the theoretical and the purity 90%.

A similar method of obtaining β-HMX was given by Robbins and Boswell [163]. The composition of the product was 77.5% HMX and 22.5% RDX. The yield of HMX was 87.5%. A method was also described for nitrating hexamine with nitric acid in the presence of BF_3. A yield of 96% was claimed [164].

Preparation of Octogen from DPT (3,7-dinitro-1,3,5,7-tetraazabicyclo [3, 3, 1] nonane) (Vol. III, p. 90, formula XII)

There are methods of obtaining octogen in two steps by forming DPT as the first step, followed by acting on DPT with nitric acid or nitric acid with ammonium nitrate or nitric acid, ammonium nitrate and acetic anhydride. However the yield of DPT is not very high.

The best method of obtaining DPT consists in introducing hexamine dinitrate to 90% sulphuric acid at 8–15°C. After 45 min. all is poured on ice and the solution is filtrated. The filtrate is neutralized with 28% ammonia to pH = 5.5–6.5 DPT precipitated [165].

Another method of making octogen from DPT (1 mole) consists in acting with NH_4NO_3 (1.6 mole) and nitric acid (3.2 mole) at 60–65°C for one hour. Water is then added and all is heated for 12 hours in a steam-bath. The yield was 75% of the theoretical (according to [5]).

The description of the industrial manufacture of octogen in Hungary has been given [166]. In the first step DPT was obtained from hexamine, acetic anhydride, paraformaldehyde and a solution of ammonium nitrate in nitric acid. After that the rest of the reagents were added.

Altogether for 1 mole of hexamine, the following reagents were added:

5–7 moles of nitric acid (min. 98%),
3–5 moles ammonium nitrate,
10–11 moles acetic anhydride and
0.27–0.54 moles of paraformaldehyde.

The reaction was carried out at 44°C.

After that water was added and the temperature was raised to 98°C by injecting live steam. All was cooled and the product filtered. It contained 60–70% octogen and 30–40% hexogen.

Tc obtain pure β-form the product is dissolved in acetone and refluxed for 45 min. All forms of octogen pass into the solution. Also unstable products decompose on boiling.

If pure octogen free of cyclonite is required, octogen can be obtained due to lower solubility in acetone. By warming the product with a three times larger quantity of acetone at 40–50°C, all cyclonite passes into the solution.

The commercial grade of HMX produced in France seems to contain *ca.* 2.25% RDX [179].

Specification for Octogen

The U.S. specification describes two grades of octogen:

Grade 1, min. 93%,
Grade 2, min. 98%.

The quantity of octogen is determined by treating an 0.2 g sample with 100 ml of 1,2-dichloroethane saturated with HMX. The insoluble matter is pure octogen.

The octogen should consist of β-polymorph by examination of a 5% mull of the sample in hexachlorobutadiene or tetrachloroethylene in a sodium chloride cell. Another sample of pure β-polymorph is placed in a compensating cell. The absorption is observed between 14.0 and 14.3 μ.

M.p. should be min. 270°C
Insoluble in acetone max. 0.05%

Inorganic insoluble max. 0.03%
Acidity max. 0.02% (as acetic acid)
Granulation is different in 5 classes.

For transportation it is kept in water-tight bags with a minimum 10% solution of 40% isopropyl alcohol and 60% water.

In the presence of RDX the quantitative determination of HMX is by the formation of the stable complex: of HMX with dimethylformamide insoluble in CCl_4. Another method consists in the separation of HMX by low solubility in 1,2-dichloroethane. For detailed description of the methods see the Encyclopedia [127].

The Soviet Union specification for octogen used for detonating fuses includes the items as follows (according to [5]):

m.p. min 278°C
critical and limiting diameters at density 1.65

should be 1 mm and 4 mm respectively.

The velocity of detonation is

8400 m/s at $\rho = 1.65$ and
8800 m/s at $\rho = 1.75$.

When heated at 335°C the induction period should be 5 s.

For other requirements referred to charges for deep bore-holes see [5].

EXPLOSIVES WITH OCTOGEN AS A MAIN COMPONENT

Price [176] gave a description of the explosive properties of octogen (91%) desensitized with wax (9%): at density 1.71 it shows the rate of detonation 8680 m/s. Octol – a castable mixture of octogen (77%) and TNT (23%) gave the rate of detonation 8540 m/s (density 1.80). They are stronger than analogous compositions with cyclonite.

Kegeler [177] described the composition of 65% octogen with 35% TNT. It shows the rate of detonation

8254 m/s at $\rho = 1.80$, and
8156 m/s at $\rho = 1.77$.

There are also compositions described, for example of 94% octogen, 3% nitrocellulose and 3% (β-chloroethyl) phosphate [178].

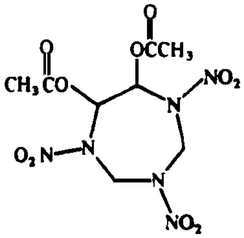
Of considerable importance now are mixtures of octogen with aluminium powder. Two papers have appeared recently on the ability of aluminized HMX to pass from burning to detonation. Langen and Barth [179] described the properties of Octal 70/30, that is, HMX (with wax) 70% and aluminium 30%. HMX with wax was composed of 95% of Höchst waxes 'S' and 'KP' in equal proportions, that is 2.5% of each. The authors of the paper described the method of mixing the ingredients as follows: 100 parts of HMX desensitized with waxes were pre-heated to 90°C, 42.9 parts of aluminium degreased with carbon tetrachloride and preheated to 90°C were mixed in a vessel connected to ground potential. After that the mixture was sieved through 1 mm mesh size. The performance of Octal 70/30 was better than that of RDX/Al 70/30. This can be seen from Table 64.

TABLE 64. Comparison of octal 70/30 with RDX/Al

	Heat of explosion kcal/kg	Lead block test cm^3
Octal 70/30	1650	555
RDX/Al 70/30	1635	470

Price and Clairmont [180] examined fine (5 μm) and coarse (95 μm) aluminium on the deflagration to detonation transition of HMX/Al pressed charges. They found that Al, particularly fine grain, increases the length of the predetonation column. However wax is more effective than Al: it is more efficient in delaying the detonation.

BSX (1,7-DIACETOXY-2,4,6-TRINITRO-2,4,6-TRIAZAHEPTANE)



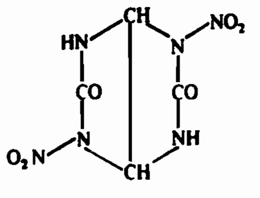
"BSX"

The compound is formed as a by-product of cyclonite when made by the method of W. E. Bachmann [158–159] and Köffler (Vol. III, p. 111).

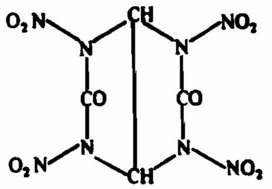
This was described by G. F. Wright [2].

The remarkable property of the compound shown by Hall [181] is its ability to form complexes: with dioxane, cyclohexanone, tetrachloroethane, formamide. All in the proportion 1:1. The complex with acetophenone is in the proportion 2:1.

DINGU AND SORGUYL



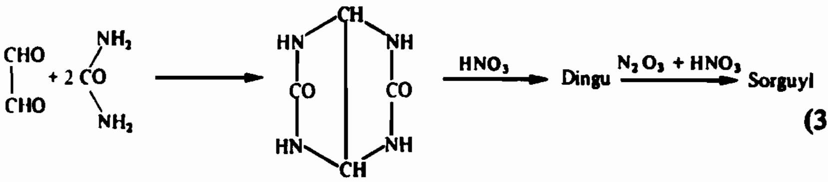
Dingu
(Dinitroglycolurile)



Sorguyl
(Tetranitroglycolurile)

French authors obtained a patent [182] for two explosive compounds: Dingu and Sorguyl.

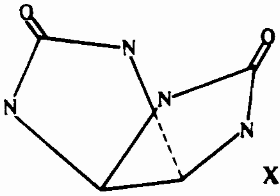
Both are obtained by the nitration of glycolurile which is formed through the action of urea on glyoxal (36).



Glycolurile

(36)

The stereochemical structure of glycolurile can be depicted by formula (XXII)



XXII

The following are data on Dingu and Sorguyl (Table 65) according to Meyer [183].

TABLE 65. Properties of Dingu and Sorguyl

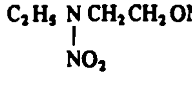
	Dingu	Sorguyl
Decomposition temperature	225–250°C (beginning 130°C)	237°C
Density	1.94	2.01
Rate of detonation	7580 m/s at = 1.75	9150 m/s at = 1.95
Oxygen balance	−27.6%	+5.0%

Dingu is relatively readily decomposed by alkaline hydrolysis, but is stable in an acid medium. It is insoluble in molten TNT, soluble in dimethylsulphoxide.

Sorguyl is remarkable by its high density, extremely high velocity of detonation, and positive oxygen balance. It is not hygroscopic but decomposes by hydrolysis. It decomposes in molten TNT.

N-NITRO-*O*-NITRO COMPOUNDS

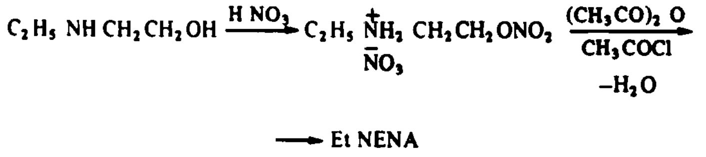
One representative of this group of compounds merits attention. This is 1-(*N*-Ethyl)-nitramino-2-ethanol Nitrate, code name Et-NENA [73]



$$C_2H_5\underset{NO_2}{\underset{|}{N}}CH_2CH_2ONO_2$$

m.p. 4.0–5.5°C

This is an oil, d = 1.32 at 25°/4°C, n_D = 1.479/25°C. It was prepared by Blomquist and Fiedorek [73, 74] from ethylaminoethanol. The latter was added dropwise to 98% nitric acid at 10°C. The resulting mixture was added dropwise to 95% acetic anhydride with some acetyl chloride to transform the nitrate salt into nitramine:



$$C_2H_5\,NH\,CH_2CH_2OH \xrightarrow{HNO_3} C_2H_5\,\underset{\bar{N}O_3}{\overset{+}{N}H_3}\,CH_2CH_2ONO_2 \xrightarrow[\substack{CH_3COCl \\ -H_2O}]{(CH_3CO)_2\,O} Et\,NENA$$

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APPENDIX

Thermal Decomposition

Thermal decomposition of dimethyl nitramine was studied by Flournoy [1], Korsunskii, Dubovitskii and co-workers [2, 3].

The decomposition occurred in two steps:

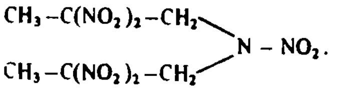
$$(CH_3)_2N{-}NO_2 \rightleftharpoons (CH_3)_2\,N\cdot + \cdot NO_2 \qquad (1)$$

$$(CH_3)_2N{-}NO_2 + NO_2 \longrightarrow \text{products of oxidation} \qquad (2)$$

Similar results were described by Korsunskii, Dubovitskii and Shurygin [4] on the decomposition of higher nitramines.

The activation energy of the decomposition of dimethylnitramine was found to be 40.8 kcal/mol and the log of frequency factor log B = 14.1.

Korsunskii, Dubovitskii and co-workers [5] studied the thermal decomposition of an interesting compound: bis-(2,2-dinitropropyl)-*N*-nitramine:

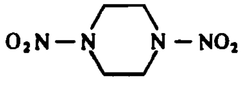


They examined the decomposition of 5% solution of the compound in *m*-dinitrobenzene at temperatures 145–196°C and found energy of activation 39.7 kcal/mol and log B = 15.7.

Thermochemistry

Pepekin and co-workers [6] examined thermochemistry of cyclic *N*-nitro compounds: dinitropiperazine and cyclonite (RDX).

The data are as below:



Cyclonite

	H_f cryst.	H_f gas
	kcal/mol	
Dinitropiperazine	−12.7	13.9
Cyclonite	14.7	45.8

Mechanism of the Nitration of Hexamine to Cyclonite (RDX) and Octogen (HMX).

The above mechanism was described in Vol. III (pp. 87–98, 113–117). It was also investigated by nuclear tracer technique with:

Hexamine	^{14}C
Paraformaldehyde	^{14}C
$^{15}NH_4NO_3$ [7].	

The result of these experiments confirmed in general the diagrams of the reactions given before.

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CHAPTER 14

EXPLOSIVE POLYMERS

With the present advent of polymer chemistry numerous efforts have been made on synthetic polymers containing nitro groups (whether *C*-, *O*- or *N*-nitro groups) with the aim of possibly replacing (or imitating) nitrocellulose and (to a much smaller extent) nitrostarch. To date it has been difficult to obtain a synthetic polymer which would possess the same mechanical properties as that of nitrocellulose.

C-NITRO POLYMERS

Nitropolystyrene and its Derivatives

In Vol. I, pp. 418–419 nitropolystyrene was described and its possible practical application is mainly in low power mining explosives and in pyrotechnic mixtures. According to [3], molecular weight is over *ca.* 38000.

An interesting polymer 'Peptidyl' was obtained by E. Katchalski and co-workers [1] which is poly-4-hydroxy-3-nitrostyrene, an improved version of the polymer used by Merrifield [2] for the formation of peptides. Peptidyl was obtained by nitrating a co-polymer of acetoxystyrene with divinylbenzene in proportion 100:4. Divinylbenzene is used as a cross-linking agent.

Nitroindene Polymer (p. 410)

Nitroindene polymer was obtained by the nitration of polyindene [3]. It is an amorphous solid of m.p. 230°C, and is insoluble in most solvents. Decomposition (explosion) temperature is above 360°C. It is slightly hygroscopic, taking 1.61% water from the atmosphere of 100% relative humidity. The International heat test at 75°C showed 1.1% loss of weight. A sample of 5 g evolved *in vacuo* 12 cm^3 of gas in 48 hours. It was considered for use in U.S. Army as a time fuse but was found to be too sensitive to impact.

POLYNITRO ALKANES

Nitroethylene Polymer (Vol. I, p. 596) $(CH_2 = CH\ NO_2)_n$

Nitroethylene was mentioned in Chapter VIII. Here the polymer will be described, according to Noma and co-workers [4], Perekalin and Sopova [5], Encyclopedia of Fedoroff and Sheffield [6], Novikov and co-workers [7].

Nitroethylene polymer is a white amorphous solid which does not melt but decomposes on heating above 75°C.

During World War II in the U.S.A. [6] a method of preparing nitroethylene was developed consisting of the action of sodium bicarbonate on 1-chloro-2-nitroethane. The yield of nitroethylene was 76%.

Polymerization was carried out in aqueous medium in the presence of an emulsifier and ascaridole (a terpene peroxide) as a catalyst. Air over the liquid was replaced by nitrogen and nitroethylene was introduced gradually to the water. The reaction ended after 2 hours of mixing.

Perekalin and his co-workers [8] have done pioneering work on the polymerization of nitroethylene under γ-radiation from Co^{60}. Perekalin *et al.* pointed out that the methods so far used to polymerize nitroethylene gave a low molecular weight of *ca.* 2000. When the polymerization was carried out in a solvent, for example, dimethylformamide or tetrahydrofurane, the molecular weight was higher but the product was still a powder, although the γ-radiation yielded a transparent product. The part which was not polymerized was subjected to further irradiation etc. and eventually a transparent block was obtained. Perekalin also found that polymerization continues after irradiation. On the basis of the latter fact he concluded that the polymer contains free radical of long life and the reaction of polymerization is a free-radical reaction. The molecular weight of polynitroethylene obtained by Perekalin *et al.* was of the order of 38000 (through measurement of viscosity) and density was 1.535. It decomposed when heated to 150°C.

In a number of papers Yamaoka and co-workers [9–14] examined polymerization. Their main conclusion was that radiation induced polymerization through the anionic mechanism involving free ions and induced post-polymerization at temperatures below −150°C.

Nitroethylene polymer is a white amorphous solid which does not melt. According to [6] it decomposed slowly at 75°C. After 2 hours of maintaining this temperature it ignited. When heated to 100°C it deflagrated with a sooty smoke in 23 min. On a hot plate of 200°C it decomposed without explosion. The sensitivity to impact is of the order of TNT. The strength (in ballistic mortar) constitutes only 29% of that of TNT. Hungarian authors [15] reported the data for polynitroethylene as follows:

heat of detonation	720 kcal/kg
lead block expansion	114 cm^3
impact sensitivity (2 kg)	70–90 cm (TNT 50–60 cm).

POLYURETHANES WITH ALIPHATIC *C*- AND *N*-NITRO GROUPS

A large number of polyurethanes were made of nitro aliphatic polymers consisting in co-polymerization of nitro aliphatic diisocyanate with nitro aliphatic diols. They were made by Aerojet General Corp., by Blatz, Gold and co-workers [16].

Two main lines were taken:

(1) to polymerize isocyanates to polyurethanes with diols (in mol. proportion 1:1) both containing *C*-nitro groups, and some of diols with *N*-nitro groups,

(2) to nitrate the above polymers ('the postnitration') to increase the number of the nitro group.

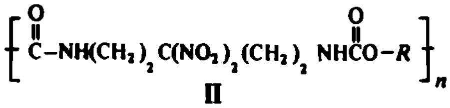
Most of the compounds are described below.

1. Co-polymers from 3,3-Dinitro-1,5-pentane Diisocyanate (I) and Nitrodiols.

$$O{=}C{=}N{-}CH_2\,CH_2C(NO_2)_2\,(CH_2)_2{-}N{=}C{=}O$$

I

The general formula (II) gives the structure with variable *R* which depends on the used nitrodiol



$$\left[\overset{\overset{O}{\|}}{C}{-}NH(CH_2)_2C(NO_2)_2(CH_2)_2\,NH\overset{\overset{O}{\|}}{C}O{-}R\right]_n$$

II

The following were compounds IIa–IIe made of I and different diols listed below (Table 66).

TABLE 66. Co-polymers of I with diols: polymer II

Compound	Name of diol	Formulae of polymers II $R=$
IIa	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
IIb	5,5,5-Trinitro-1,2-pentanediol	$-OCH_2-\overset{\overset{O-}{\vert}}{C}H(CH_2)_2-C(NO_2)_3$
IIc	2,2,4,4-Tetranitro-1,5-pentanediol	$-CH_2-C(NO_2)_2-CH_2-C(NO_2)_2-CH_2O-$
IId	4,4,6,8,8-Pentanenitro-1,11-undecanediol	$-(CH_2)_3-C(NO_2)_2-CH_2-CH(NO_2)-CH_2-C(NO_2)_2-(CH_2)_3O-$
IIc	4,4,6,6,8,8-Hexanitro-1,11-undecanediol	$-(CH_2)_3-C(NO_2)_2-CH_2-C(NO_2)_2-CH_2-C(NO_2)_2-(CH_2)_3O-$
IIf	5,7,9-Trinitro-5,7,9-triaza-3,11-dioxa-1,13-tridecanediol	$-(CH_2)_2OCH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)-CH_2-O(CH_2)_2O-$

Another group of polymers with the same diisocyanate (I) was reacted with diamine (III) to form polymer (IIIa) which is a urea derivative:

$$\mathrm{NH_2(CH_2)_2C(NO_2)_2(CH_2)_2NH_2}$$

III

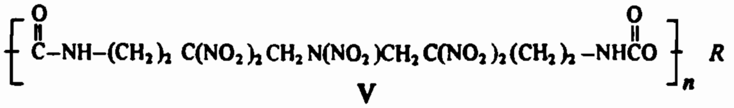
$$\left[\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH(CH_2)_2C(NO_2)_2(CH_2)_2NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH(CH_2)_2C(NO_2)_2(CH_2)_2NH}\right]_n$$

IIIa

Another series of polymers were made from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate (IV) and diols. The general formula of polymers is V and the compounds are listed in Table 67.

$$\mathrm{O{=}C{=}N{-}(CH_2)_2C(NO_2)_2CH_2\,N(NO_2)CH_2C(NO_2)_2\,(CH_2)_2{-}N{=}C{=}O}$$

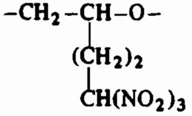
IV



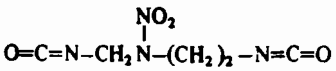
$$\left[\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}NH{-}(CH_2)_2\,C(NO_2)_2CH_2N(NO_2)CH_2C(NO_2)_2(CH_2)_2{-}NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]_n R$$

V

TABLE 67. Co-polymers of IV with diols: polymers V

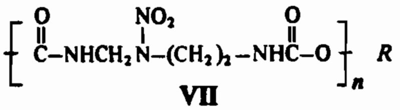
Compound	Name of diol	Formulae of Polymers V *R*=
Va	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
Vb	5,5,5-Trinitro-1,2-pentanediol	 $-CH_2-\underset{\underset{CH(NO_2)_3}{\mid}}{\underset{(CH_2)_2}{\underset{\mid}{CH}}}-O-$

Three co-polymers were made from 2-Nitraza-1,4-butane Diisocyanate (VI) with diols to form polymers VII:



$$\mathrm{O{=}C{=}N{-}CH_2}\overset{\mathrm{NO_2}}{\overset{\mid}{\mathrm{N}}}\mathrm{{-}(CH_2)_2{-}N{=}C{=}O}$$

VI



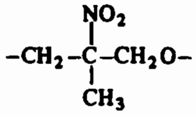
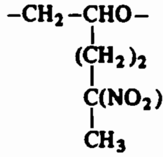
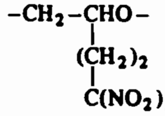
$$\left[\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}NHCH_2}\overset{\mathrm{NO_2}}{\overset{\mid}{\mathrm{N}}}\mathrm{{-}(CH_2)_2{-}NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}O}\right]_n R$$

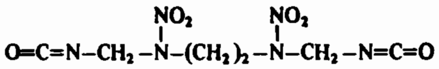
VII

Their formulae are given in Table 68.

Two co-polymers were made of 2,5-dinitraza-1,6-hexane diisocyanate (VIII) and diols which led to polymers (IX):

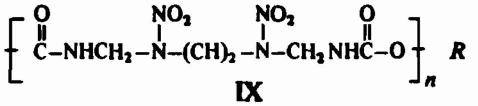
TABLE 68. Co-polymers of VI with diols: polymers VII

Compound	Name of diol	Formulae of Polymers VII *R*=
VIIa	2-Nitro-2-methyl-1,3-propanediol	 $-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{NO_2}{\vert}}{C}}-CH_2O-$
VIIb	5,5-Dinitro-1,2-hexanediol	 $-CH_2-\underset{\begin{array}{l}\vert\\(CH_2)_2\\\vert\\C(NO_2)_2\\\vert\\CH_3\end{array}}{C}HO-$
VIIc	5,5,5-Trinitro-1,2-pentanediol	 $-CH_2-\underset{\begin{array}{l}\vert\\(CH_2)_2\\\vert\\C(NO_2)_3\end{array}}{C}HO-$



$$O{=}C{=}N-CH_2-\overset{\overset{NO_2}{|}}{N}-(CH_2)_2-\overset{\overset{NO_2}{|}}{N}-CH_2-N{=}C{=}O$$

VIII

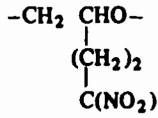


$$\left[\overset{\overset{O}{\|}}{C}-NHCH_2-\overset{\overset{NO_2}{|}}{N}-(CH)_2-\overset{\overset{NO_2}{|}}{N}-CH_2NH\overset{\overset{O}{\|}}{C}-O\right]_n R$$

IX

The formulae of IX are given in Table 69.

TABLE 69. Co-polymers of VIII with diols: polymers IX

Compound	Name of diol	Formulae of Polymers IX *R*=
IXa	2,2-Dinitro-1,3-propanediol	$-CH_2-C(NO_2)_2-CH_2O-$
IXb	5,5,5-Trinitro-1,2-pentanediol	 $-CH_2\ \underset{\begin{array}{l}\vert\\(CH_2)_2\\\vert\\C(NO_2)_3\end{array}}{C}HO-$

All polymers show the relative viscosity of 1% acetone solution between 1.1 and 1.8 cp. Partial compatibility with nitrocellulose and rubber has been described for polymers IIc and IId. The densities of samples II were 1.50–1.64. Polymer IIa showed explosive properties; it detonated with the rate of 6200 m/s at d = 1.57.

The sensitivity of the melting points to impact and stability are given in Table 70.

TABLE 70. Some properties of co-polymers: diisocyanates–diols

Compound	m.p. °C	Impact sensitivity* RDX = 28 cm cm	Stability	
			134.5°C methyl violet min	65.5 KI-starch, min
IIa	75–78	100	195	300
IIb	85–95	85	78	10
IIc	70–80	80–85	13	12
IId	*ca.* 40	100	10, Expl. 22	11
IIe	40	100	Expl. 8	8
IIf	55–60	80–85	300	300
IIIa	110–115	80–85	75	300
Va	75–85	40		13
Vb	65–75	65		20
VIIa	90–100	100		300
VIIb	70–80	100		390
VIIc	80–90	55		38
IXa	85–95	100		90
IXb	90–100	60		10

* Impact sensitivity is expressed in the height of 2 kg weight giving 50% probability of explosions comparing with the standard-Cyclonite (RDX) which requires 28–35 cm height.

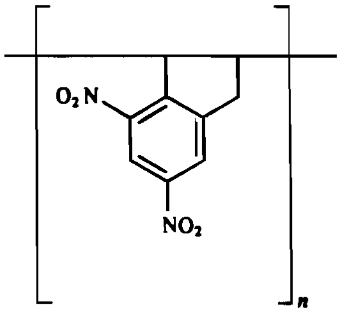
Preparation

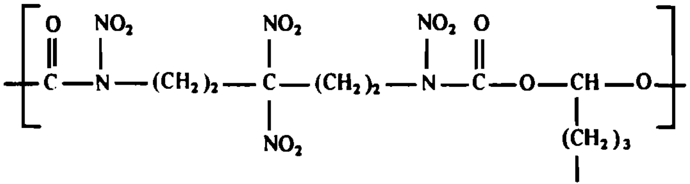
Polymers were prepared by adding dropwise a solution of a diol and a catalyst in absolute dioxane to an equivalent amount of a diisocyanate at 20 to 50°C depending on the substances used. The catalyst in all instances (with the exception of IId and e) was ferric acetylacetonate in quantity of 0.05–0.15% in relation to the diol. With IId and IIe it was boron trifluoride–ether complex in proportion of *ca.* 1.5 mol %. The temperature was kept at 20–40°C for a longer time: from 2 days to several weeks. At the end the temperature should be raised to 50°C. The product was precipitated by adding water. The solvent was removed by steam distillation or by vacuum drying. The yield in most instances was of the order of 95% (with IIf it was *ca.* 44%).

It can be seen from Table 70 that some of the polymers possess poor stability but show low sensitivity to impact. Some of them are remarkably stable at 134.5°C.

2. *Nitration of polyurethanes containing nitro groups [16].* Several polyurethanes described above have been subjected to nitration. However, most of the products show poor stability. The previously described IIb was nitrated with 100% nitric acid at room temperature followed by gradually raising the tempera-

ture to 50°C and keeping it for 20 min. The product (X) was obtained by pouring on ice and vacuum drying the precipitated product. The impact sensitivity was 30 cm (RDX 28 cm), heat test (with KI) 5 min at 65.5°C and the relative viscosity was 1.6 cp at 25°C for 2% solution in acetone.


Nitroindene
polymer
(p.404)



$$\left[-\overset{O}{\overset{\|}{C}}-\overset{NO_2}{\overset{|}{N}}-(CH_2)_2-\underset{NO_2}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}-(CH_2)_2-\overset{NO_2}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-\underset{C(NO_2)_3}{\underset{|}{\underset{(CH_2)_3}{\underset{|}{CH}}}}-O-\right]$$

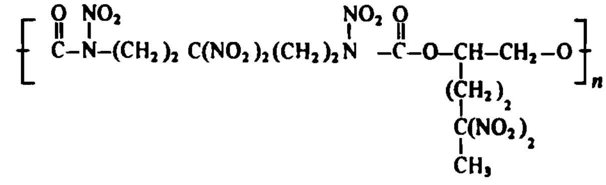
X

Some co-polymers of urethanes with diols after the nitration could also not stand the test at 134.5°C. One of them exploded after 11 min of heating.

The exception from the point of view of stability shows the nitrated polymer made of I and 5,5-dinitro-1,2-hexanediol. It is an amorphous powder, m.p. 55–65°C (XI) and is soluble in acetone. The polymer was prepared in two steps:

(a) the monomers were dissolved in dioxane and kept at 50°C for *ca.* 24 days. The product was precipitated with water.

(b) The polymer was nitrated with 100% nitric acid at 0°C. It was precipitated with water. The yield was 97%.

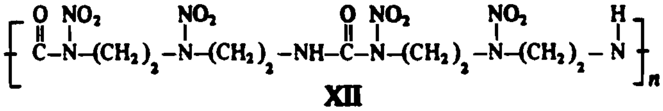


$$\left[\overset{O}{\overset{\|}{C}}-\overset{NO_2}{\overset{|}{N}}-(CH_2)_2\,C(NO_2)_2(CH_2)_2\overset{NO_2}{\overset{|}{N}}\,-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\underset{|}{\underset{C(NO_2)_2}{\underset{|}{\underset{(CH_2)_2}{\underset{|}{CH}}}}}}-CH_2-O\right]_n$$

XI

Impact sensitivity was 100 cm (RDX 28 cm). Thermal stability: at 65.5°C (KI paper) 23 min, at 134.5°C no decomposition (methyl violet paper) in 5 hours.

Another product which may show some promise with regard to stability is nitrated urea derivative (XIV)



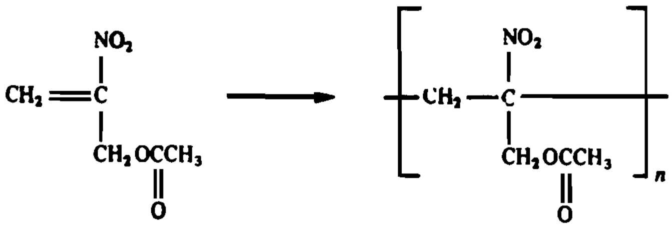
$$\left[\overset{O}{\overset{\|}{C}}-\overset{NO_2}{N}-(CH_2)_2-\overset{NO_2}{N}-(CH_2)_2-NH-\overset{O}{\overset{\|}{C}}-\overset{NO_2}{N}-(CH_2)_2-\overset{NO_2}{N}-(CH_2)_2-\overset{H}{N} \right]_n$$

XII

It is an amorphous solid, m.p. 80–90°C which was obtained by hydrolysing 3-nitro-3-aza-1,5-pentane diisocyanate with water followed by nitration.

C-NITRO POLYMERS FROM MONOMERS WITH A VINYL GROUP

Nitroallyl Acetate Polymer [3]



XIII

The monomer – nitroallyl acetate can be obtained from methyl nitrate and formaldehyde, followed by esterification and oxidation (1):

$$\begin{gathered} CH_3ONO_2 + 2CH_2O \xrightarrow{\text{(gas phase)}} CHNO_2(CH_2OH)_2 \xrightarrow{CH_3COOH} \\ CHNO_2(CH_2OOCCH_3)_2 \xrightarrow{[O]} \underset{\text{XIII}}{CH_2{=}C(NO_2){-}CH_2COOCH_3} \end{gathered} \qquad (1)$$

The monomer has m.p. 17.5°C, b.p. (at 2 mmHg) 68°C.

It polymerizes on exposure to air at room temperature. The stability does not seem to be satisfactory – an explosion occurred after 10 min of keeping at 134.5°C.

Ethyl Nitroacrylate

$$NO_2\,CH = CH\,COOC_2H_5$$

The compound was obtained by Yanovskaya, Stepanova and Kucherov [17] from formylacrylic acid ester and nitromethane. No information was given on the possible polymerization of the compound.

Nitroethyl acrylate

$$\mathrm{CH_2 = CH{-}COO\,CH_2CH_2NO_2}$$

b.p. 100°C (5 mmHg)

This was one of the most simple acrylates obtained by Marans and Zelinski [18] (see also Chapter VIII). It can polymerize under the action of benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a soft, viscous resin (contrary to the polymer of methacrylate which is hard).

Nitroethyl Methacrylate [18]

$$\mathrm{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COO\,CH_2CH_2NO_2}$$

b.p. 115°C (10 mmHg)

The compound gives a polymer when catalysed by benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a hard resin.

Trinitroethyl acrylate

$$\mathrm{CH_2{=}CH{-}COOCH_2C(NO_2)_3}$$

b.p. 80°C (2 mm)

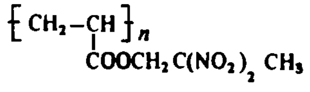
This was obtained by Ville [19] by acting with acrylyl chloride on 2-trinitroethanol (Chapter VIII). No information was given on the possible polymerization.

Dinitropropyl Acrylate (DNPA) [3]

$$\mathrm{CH_2{=}CH\,COO\,CH_2C(NO_2)_2CH_3}$$

m.p. 175°C, b.p. 96°C (0.2 mmHg)

The monomer was prepared by dissolving 2,2-dinitropropanol and acrylic chloride in carbon tetrachloride and heating for 12 hours at 55°C. The dried product was mixed with powdered silver and vacuum distilled. It can be used as a binder in propellants burning readily at a pressure of *ca.* 70 kg/cm^2. It can be polymerized in toluene in the presence of azobisisobutyronitrile as a free radical catalyst, under dry nitrogen at 80°C for 45 min. The conversion of 25% was obtained to yield the polymer:

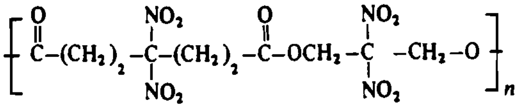


$$\left[\mathrm{CH_2{-}\underset{\displaystyle COOCH_2C(NO_2)_2\,CH_3}{\underset{|}{CH}}}\right]_n$$

Poly-DNPA has an explosion temperature at 250°C, the detonation rate of 6100 m/s [19].

POLYESTERS OF DINITROCARBOXYLIC ACIDS AND DINITRODIOLS

The polymer of 4,4,-Dinitro-1.7-Heptanediolcarboxy Chloride and 2.2.-Dinitro-1,3-Propanediol was described [20]:



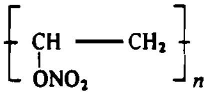
$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\underset{NO_2}{\overset{NO_2}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-OCH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The molecular weight of the polymer was 4000–9000, i.e. $n = 11–24$. It is a yellow coloured powder of m.p. 180–185°C.

It was prepared by dissolving equivalent amounts of the monomers in dioxane followed by maintaining the temperature of 30°C for 3 days. The solution was filtered, poured into water with ice and vacuum steam distilled to obtain the product. It shows a low sensitivity to impact: 2 kg at 85–95 cm (RDX 28 cm), and a good stability: at 65.5°C (KI paper) is 100 min, at 134.5°C (Methyl violet paper) – 80 min.

POLYMER WITH *O*-NITRO GROUPS

Polyvinyl Nitrate (PVN) (Vol. II, p. 173)



$$\left[-\underset{ONO_2}{CH}-CH_2-\right]_n$$

The polymer originally created certain hopes that it could replace (partly at least) nitrocellulose. The problem remains unsolved although a considerable amount of information on PVN was collected.

The following are references which should be added to those mentioned in Vol. II: Frank and Krüger [21], Chédin and Tribot [22], Auberstein and Laford [23], Akopyan and co-workers [24].

Properties of PVN

Chemical and physical properties. A rather detailed description of PVN can be found in the paper by Diepold [25]. Here are the data on properties of PVN according to this author:

Nitrogen content N 15.15% (which indicates the degree of esterification 92.8%). The other sources [29] gave 15.7% which is practically 100% nitration (99.8%).

Molecular weight M_w	200 000,
Viscosity of 0.5% solution in acetone at 25°C	0.45 cP
Included (or adsorbed) acidity	less than 0.005% HNO_3
Insoluble (in acetone)	max. *ca.* 1%
Colour	yellowish white
Size of grains	less than 1 mm
Density	1.6
Free flowing density	0.3

Hygroscopicity at 30%/90% relative humidity was 0.62% [27]

Softening temperature	30–40°C
Freezing temperature	30°C

Strength:

Temperature °C	On stretching	Breaking elongation
–40°	500 bar	0.4%
+20°	450 bar	0.8%
+40°	20 bar	400%

The plastic properties of PVN plastified with dibutyl phthalate or bis(2-fluoro-2,2-dinitroethyl) formal was examined by Michaud and co-workers [26] through pulsed NMR analysis. The purpose of this study was to find the different phases and to examine them in a function of concentration and temperature. The following were the phases found in the plasticized PVN: (1) a rigid polymer, (2) a mobile polymer, (3) a rigid plasticizer and (4) a mobile plasticizer. The work has a general significance on the insight of the nature of plastification and mobility of macromolecular chains and on the nature of the plastic flow and exudation.

Explosive Properties (according to [25])

PVN (15.15% N) shows the temperature of decomposition:

195°C when heated at the rate of 20°C/min,
177°C when heated at the rate of 5°C/min.

The induction period is 7 min and over 18 hours at 175° and 165°C respectively. According to Picatinny Arsenal [27] PVN (14.86% N) gives an explosion after 5 sec at 265°C.

The sensitivity to impact was 95 cm from a weight of 1 kg.

It is easily ignited and burns readily at the rate of 3 mm/s under pressure of *ca.* 6 kg/cm^2. The velocity of detonation slightly differs from those given in Vol. II, p. 173 [28] and according to [25] is:

density 0.3	*ca.* 3200 m/s
0.8	*ca.* 3500 m/s
1.5 (pressed)	*ca.* 6500 m/s
1.5 (cast)	*ca.* 7000 m/s.

Lead block of Trauzl 330 cm^3.

The thermochemical data are as below:

Heat of explosion 960 kcal/kg [25] and 900 kcal/kg [27]
Heat of combustion 3016 kcal/kg [25] and 2960 kcal/kg [27]
Temperature of explosion 2560°C
Volume of gases 930/kg.

Stability was determined as the loss of weight of 0.3–0.4% at 75°C for 48 hours.

Picatinny Arsenal gave the following information on stability:

Heat test (KI) at 65.5°C was over 60 min., at 134.5°C (Methyl violet) 20 min., red fumes after 25 min., explosion after more than 5 hours.

The solubility of PVN largely depends on the degree of polymerization and hence on the viscosity. The larger the viscosity the lower the solubility.

The chemical stability of PVN was extensively studied by Poulain, Michaud and Poulard [29]. They examined polymers with the molecular weight M_w and molecular number M_n of the order of 150,000–320,000 and 120,000–140,000 respectively. They aged PVN at 90° and 65°C. They followed: (1) the decomposition of the nitrate groups, (2) the degradation of the chains followed by chromatography.

As much as (1) follows the usual trend of decomposition of nitrate esters including nitrocellulose, (2) offers a much more complicated picture which differs from that of nitrocellulose. This is the observation that during heating the length of chain of PVN decreases followed by a cross-linking. (Neither length of chains or cross-linking occurs during the ageing of nitrocellulose). This is depicted in Fig. 63 referred to PVN.

The French authors [29] also examined the stabilizing action of 2-nitrodiphenylamine upon PVN. The character of ageing at 90°C was not changed by the presence of the stabilizer.

Preparation of Polyvinyl Nitrate

Le Roux and Sartorius [28] (Vol. II, p. 173) gave the following method of nitrating polyvinyl alcohol.

Five parts of polyvinyl alcohol (containing 10% of moisture) were introduced during *ca.* one hour into 100 parts of nitric acid (99–100%) at –8°C. The result-

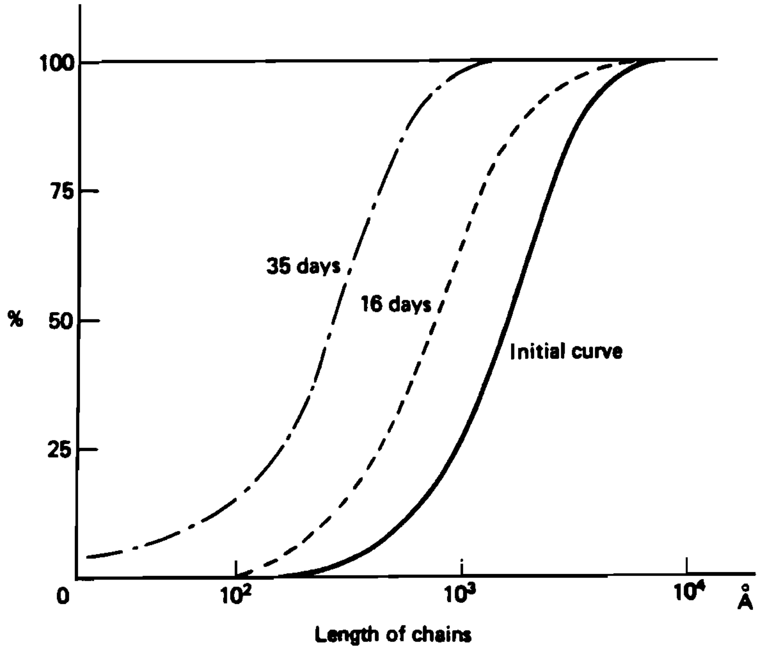


FIG. 63. Ageing of solutions of Polyvinyl Nitrate (PVN).

ing slurry was mixed for two hours and all was drowned into water with ice. The PVN white powder was washed with water to neutrality and left under water for 12 hours. The operation and standing for 12 hours was repeated with ethanol and eventually with 12% sodium bicarbonate solution. Final washing with water and drying yielded 96% of PVN.

The authors found that the determination of nitrogen in PVN in a nitrometer or by the Kjeldahl method did not give reliable results. It was necessary to use the Dumas method. According to Diepold [25] the method of titration with Fe II also gives reliable results.

The method of nitrating PVA at Picatinny Arsenal, U.S.A. [27] was as follows:

PVA was mixed with acetic anhydride, the mixture cooled to −5°C, a large excess of nitric acid was added keeping the temperature below 20°C. All was poured into cold water. The product was collected and purified by boiling in frequently changed water.

Diepold [25] described two methods of nitrating PVA: with nitric acid alone and with nitric acid/sulphuric acid mixtures.

Nitration with nitric acid. PVA was dissolved in nitric acid in proportion: Acid/PVA more than 20:1, otherwise the viscosity of the solution in nitric acid is too large to have an efficient mixing. The concentration of nitric acid should not be lower than 95%. The temperature should be kept near 0°C and the time: 15 min for introducing PVA into the acid, 30 min for the nitration and 15 min after the nitration at 20°C. The product was precipitated by pouring into water with ice. The yield was 90% of PVN with 14.8% N (the degree of nitration 88.7%), and the spent acid contained 50% HNO_3. This method does not seem to be sufficiently economic.

Nitration with nitric acid–sulphuric acid. The addition of a small proportion of sulphuric acid to nitric acid prevents dissolving PVA in nitric acid. A suspension of PVA in nitric/sulphuric acid mixture is formed. The yield of PVN is best when the concentration of H_2SO_4 in the mixed acid is 10–30% (Fig. 64). In such a mixed acid the solubility of PVN is negligible and the only substances dissolved in the acid are some degradation viscous products in quantity of 2–3%. They can be precipitated with water.

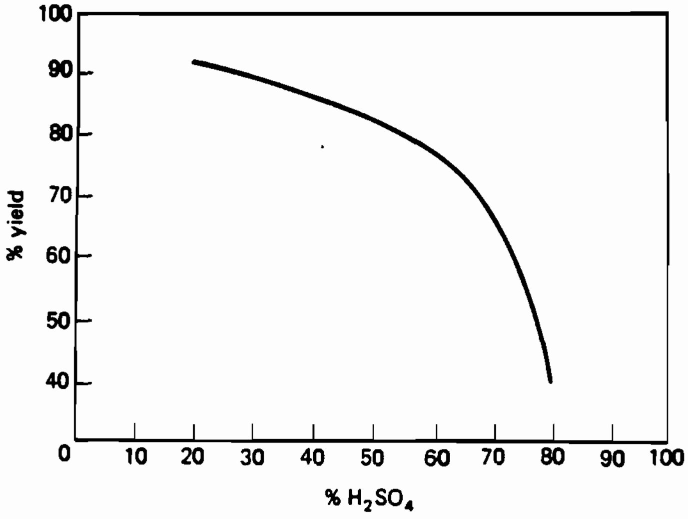


FIG. 64. Yield of PVN against the concentration of sulphuric acid in the mixed acid: $HNO_3 + H_2SO_4$.

A continuous method of nitrating PVA was described [30]. Owing to high viscosity of the solution the danger of overheating in some parts of the nitrator exists and: (1) a specially good mixing should be introduced, (2) the nitrating acid should be pre-cooled to −10°C. After the nitration is completed it is necessary to decant the acid which contains the above mentioned degradation products and to treat the product (free of the greater part of the acid) by adding water. The PVN formed fine hard grains which can be readily filtered.

The purification and stabilization of the PVN was carried out by washing the acid product with water of 60°C. At this temperature the product can soften and the grains can stick together. By adding some substances (the nature of which have not been disclosed) the sticking can be prevented and washing can be carried out even with boiling water. After the greater part of the acid has been removed the PVN should pass through a mesh filter to reduce the size of the grains and to make the removal of the last traces of the acid absorbed by PVN possible. The final product after the removal of water contained 60–70% water.

Diepold [25] gives the data as follows:

M_n	60,000–100,000
Nitrating mixture HNO_3 (1.51) H_2SO_4 (1.84)	90:10 to 70:30
Nitration temperature	0–10°C
Time of nitration	5–15 min
Stabilization	25–40 hours at 60°C.

The yield under these conditions should be 90% and the product should contain 14.8–15.1% N (i.e. degree of the nitration 88.7–92.2%).

A patent exists [31] for stabilizing PVN by dissolving the raw, decomposable PVN in an organic solvent which will be neutralized and then PVN, free of acid, will be precipitated by adding water. Calculations should be made to see whether the method is economically feasible.

Practical Use of Polyvinyl Nitrate

Experiments were carried out on PVN as a component of double base propellants PVN being used instead of nitrocellulose. *Encyclopedia of Explosives* [27] gives two compositions:

(1) with 82.0% PVN, 10.2% Nitroglycerine, 0.7% Dinitrotoluene, 6.1% Dibuthylphthalate 1.0% Diphenylamine,
(2) with 57.75% PVN, 40% Nitroglycerine, 1.5% KNO_3, 0.75% Ethyl Centralite.

Heat of explosion of these propellants was much the same as with nitrocellulose instead of PVN. However, the mechanical properties are different: decrease of tensile strength, increase of elongation at break and of flexibility. PVN did not change the burning rate, but increased the pressure exponent n ($V = k\,p^n$). Another disadvantage was that:

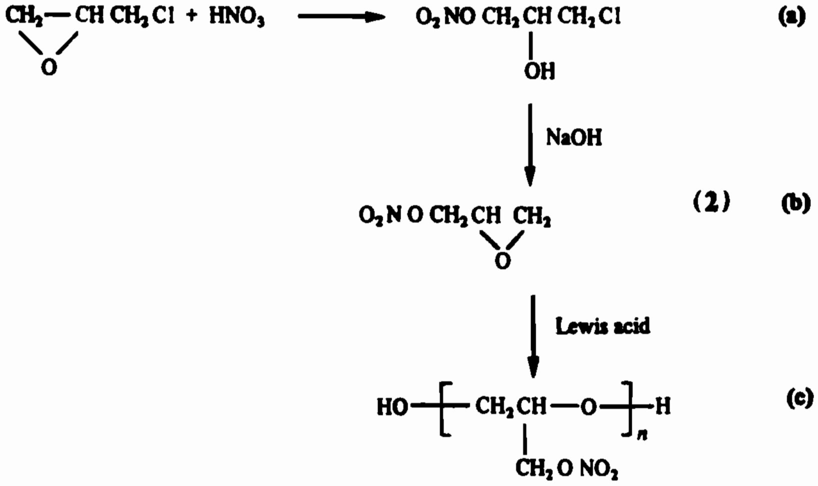
(1) atactic PVN which has a low melting point has a tendency to flow when mixed with other substances, (2) atactic PVN possesses a sticky nature which has created problems in extruding and shaping propellant grains.

The problem arises of how to obtain the isotactic polymer of PVN with high regularity and higher crystallinity. However, this does seem to be possible [32].

Modifications of Polyvinyl Nitrate

A Naval Powder Factory in the U.S.A. investigated the preparation of polyvinyl nitrate by nitration of polyvinyl acetate using epichlorohydrin as a cross-linking agent – according to Cohen [33].

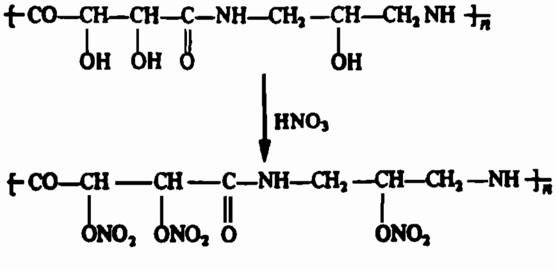
The same source [33] informs us that the U.S. Naval Ordnance Test Station and Jet Propulsion studied the preparation and polymerization of glycidyl nitrate:



(2)

n – was 20–50 and hydroxyl terminated polymers could be cured with mixtures of diol, triol and diisocyanates.

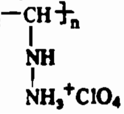
The Naval Powder Factory, according to [33] obtained *O*-nitro polymers of a relatively low molecular weight:



$$\left[-CO-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-NH-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2NH-\right]_n \xrightarrow{HNO_3} \left[-CO-\underset{ONO_2}{\underset{|}{CH}}-\underset{ONO_2}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-NH-CH_2-\underset{ONO_2}{\underset{|}{CH}}-CH_2-NH-\right]_n \quad (3)$$

HYDRAZINE AND DIFLUOROAMINE POLYMERS

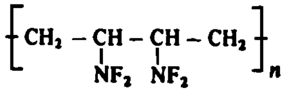
According to Cohen [33] (Bell Aerosystem Corp. and Food Machinery Corp.) obtained polyethylene hydrazine perchlorate (XIV)



$$\left[-CH_2-\underset{\underset{NH_3^+ClO_4^-}{|}}{\underset{NH}{\underset{|}{CH}}}-\right]_n$$

XIV

Information is given by the same source on a polymer with difluoroamino groups (XV) obtained by Rohm and Haas Corp.



$$\left[CH_2-\underset{NF_2}{CH}-\underset{NF_2}{CH}-CH_2 \right]_n$$

XV

Pentaerythritol trinitrate (PETriN) is a convenient source of polymers through the esterification with unsaturated vinyl group containing acids, such as acrylic and methacrylic acid.

The monomers were described in Vol. II, p. 191 and Chapter X.

N-NITRO POLYMERS

A few polymers with *N*-nitro compounds were described in Chapter XIII of this book: formulae (17) and (19).

PLASTIC BONDED EXPLOSIVES (Vol. III, p. 203)

A considerable number of explosives are composed of Cyclonite and HMX and non-explosive plastic (usually thermoplastic) polymers. Some recent compositions are given below on the basis of the literature [34]:

	Density	Rate of detonation m/s
1. Cyclonite/Polyamide resin 90/10	1,79	8390
2. HMX/DNPAF/Polyurethane (DNPAF is acetyl-formyl-2,2-dinitropropanol)	1,84	8830
3. HMX/Teflon 90/10	1,86	8640
4. HMX/Polyethylene 92/8	1,72	8630

5. American plastic explosive:
Cyclonite/Polyisobutylene/2-ethylhexyl sebacate/mineral oil in proportions 91/9.1/5.3/1.6 does not lose its plasticity at −54°C and retains its shape at +75°C.
6. British 'flexible' explosive SX-2 [35]:
Cyclonite/polyisobutylene/Teflon in proportions 88/10.5/1.5 retains its plasticity at −58°C.

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CHAPTER 15

RECOVERY OF SPENT ACIDS

(Vol. II, P. 83)

The problem of recovery of spent acids has existed since the advent of nitration of glycerine and the problems of safety related to keeping the spent acid which contained a certain amount of nitroglycerine (Vol. II, p. 84, Fig. 26). The separation of nitroglycerine which can float on the surface of the spent acid created a safety problem. The method of Nathan, Thomson and Rintoul (Vol. II, p. 85) increased safety by preventing the formation of nitroglycerine on the surface. Although a small proportion of nitroglycerine is lost by solution and decomposition, the economy is satisfactory, as no costly investment is needed for the recovery of nitroglycerine from the spent acid.

However the methods being used at present for the manufacture of nitroglycerine, such as batch combined process (Vol. II, p. 95) and all continuous processes (Vol. II, p. 97) require that spent acid be dealt with correctly. Originally primitive arrangements were in use consisting in distillation of nitric acid and careful decomposition of organic products dissolved in the spent acids.

The progress was considerably speeded up with the advent of cast silicon iron as the main acid-resistant metal [1]. Some other modern materials were also introduced into the construction of the equipment, such as enamel, tantalum, teflon [1] and glass [2]. Generally speaking the spent acid from nitration of glycerine, glycols and pentaerythritol have a lot in common although they differ in some particular points. The common problems of by-products of the nitration of alcohols will be discussed below.

GENERAL PROBLEMS OF SPENT ACID FROM THE NITRATION OF ALCOHOLS

This particular problem was studied by Camera, Zotti and Modena [3, 4]. They identified some of the products of the action of nitrating acid on ethyl nitrate as a model for the behaviour of nitrate esters in acid solution. They came to the conclusion that the initial process consisted in hydrolysis of the ester. The hydrolytic equilibrium was disturbed by oxidation of the alcohol by liberated nitric acid. In the instance of ethyl nitrate the freed ethanol was oxidized to acetaldehyde. Some other products were also formed. Nitric acid was reduced to nitrous acid which can serve as a catalyst of a number of reactions. Among the other products formed were: acetic and oxalic acids, carbon dioxide and nitrogen oxides from nitrous acid: NO_2, NO, N_2O and nitrogen.

Spent Acid from Nitration of Glycerine

According to Plinke [1] the average composition of spent acid of nitroglycerine is

HNO_3	10%
H_2SO_4	70%
H_2O	17%
Nitroglycerine	3%

Compared with the composition given in Vol. II, p. 84 it differs only by the presence of 3% of nitroglycerine. This should be regarded as all organic matters deriving from the nitration of glycerine, the hydrolysis of nitroglycerine, oxidation of the resulting mixtures etc., much in terms of the work of Camera *et al.* [3, 4].

There are three known methods of dealing with nitroglycerine spent acid:

(1) Stabilization or
(2) denitration of the acid [1],
(3) re-use of nitrating acid after adding nitric acid [5].

1. Stabilization of Spent Acid according to Plinke [1]

This method is applied when the spent acid has to be re-used without the danger of keeping it for any length of time. To destroy nitroglycerine and organic impurities the acid is conveyed at a high temperature through a number of columns where nitroglycerine and other organic substances are oxidized by nitric acid. Nitric acid is reduced to nitric oxides which are directed to the absorption column washed with water yielding dilute nitric acid.

The diagrammatic presentation of the apparatus is given in Fig. 65. Nitrator (1) is fed with nitrating mixture and glycerine, nitroglycerine is separated (7) from the spent acid which enters columns (2–4). The columns are heated with steam through a heat exchanger (9). The acid freed of oxidized organic substances is cooled in (10) and flows out. Gaseous products – mainly nitrogen oxides and carbon dioxide – pass through a cooler (11) and enter column (5). Air is blown (8) into the column where cold water (12) circulates through a pump (6) and is injected additionally to the top of the column (5). Dilute nitric acid flows from the column.

2. Denitration of Spent Acid

(A) According to Plinke [1]. The spent acid can be denitrated without adding

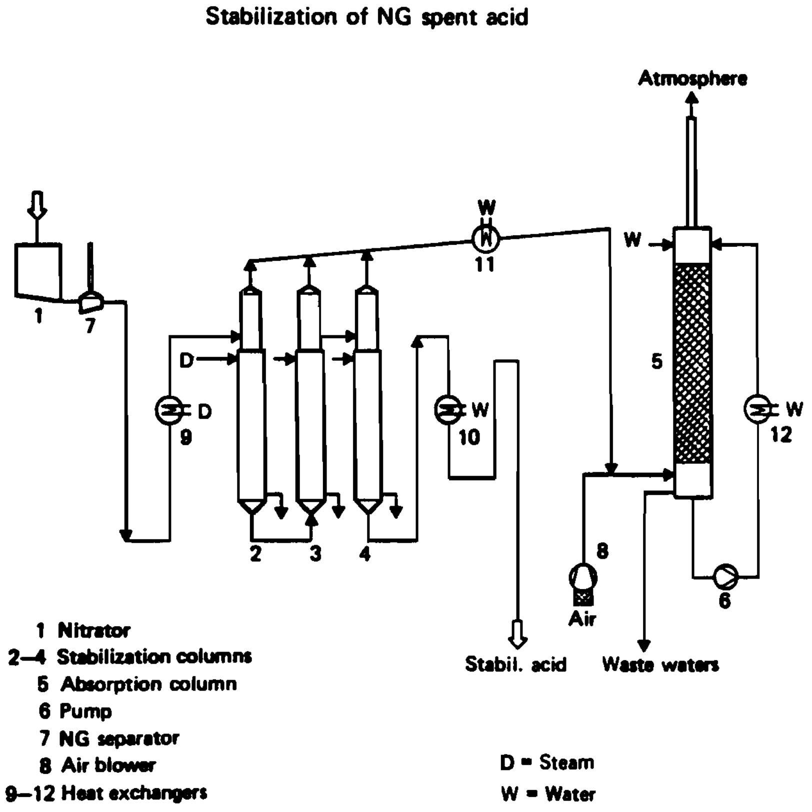
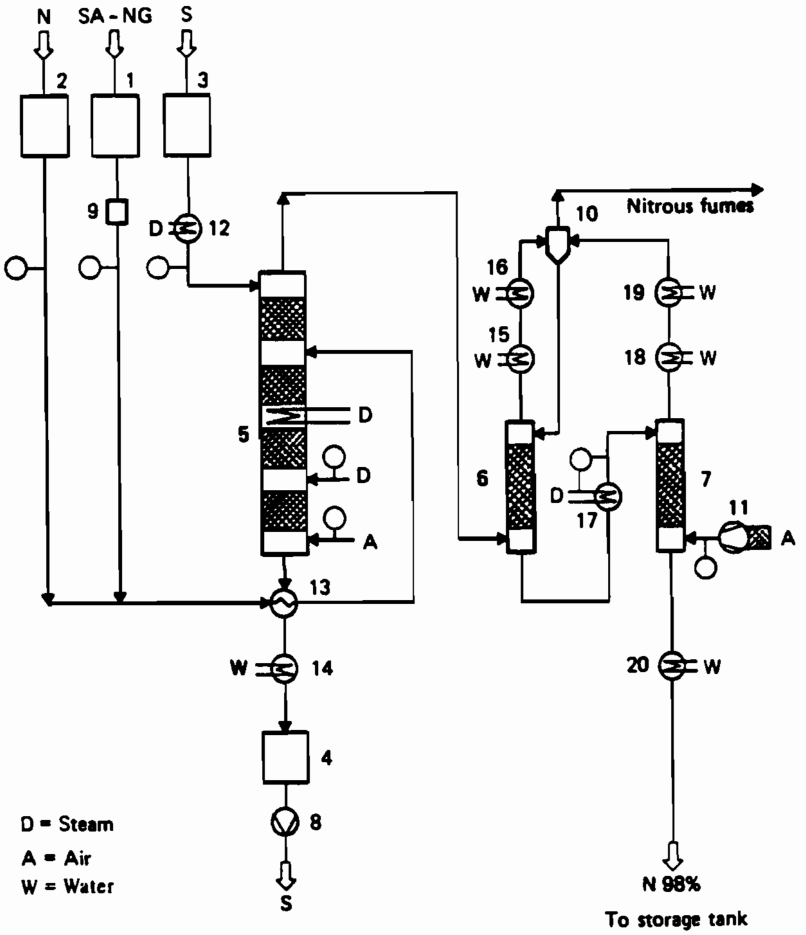


FIG. 65. Stabilization of spent acid of glycerine nitration. (Courtesy H. Plinke [1].)

other acids and nitric acid of 10% can be obtained. By adding sulphuric acid of 85–96% and (in some cases) 60% nitric acid a highly concentrated nitric acid of 98% HNO_3 can be obtained and sulphuric acid of 70% H_2SO_4. All organic compounds are destroyed and gases from decomposition (nitric oxides, nitrogen, carbon dioxide) are liberated from pre-bleaching and bleaching column. The scheme for the treatment of spent acid is given in Fig. 66.

Spent acid from (1) after separation of nitroglycerine (9) enters denitration column (5). If necessary, some nitric acid (60% HNO_3) is added from container (2). Sulphuric acid (85–96% H_2SO_4) is fed from container (3) to the top of the denitration column (5). The temperature of the denitration column is controlled by injecting steam and air. Sulphuric acid (68–72% H_2SO_4) freed of nitric acid and gaseous products is collected in tank (4) and pumped out (8). Distilled nitric acid enters pre-bleaching column (6) where it is freed of nitrogen oxides through dephlegmator (10). Pre-bleached nitric acid enters bleaching column (7) where air is blown through (11) to free the acid from the traces of nitric oxides entering

Denitration of spent acid NG



1	Feeding tank for SA - NG
2	Feeding tank for N 60%
3	Feeding tank for S 96–85%
4	Buffer tank for S 70%
5	Denitration column
6	Pre-bleaching column
7	Bleaching column
8	Pump for S 70%
9	NG - separator
10	Drop-separator
11	Ventilator air
12 -20	Heat exchangers

FIG. 66. Denitration of spent acid of glycerine nitration. (Courtesy H. Plinke [1].)

through (10). Here nitric acid flows back to column (6) and gases are blown into the air. A system of heat exchangers (12–20) serves for heating or cooling and keeps the proper temperature – high or low. Nitric acid of 98 HNO_3 flows through valve N 98 to a tank. After bleaching nitric acid contains less than 0.1% nitrous acid.

General views of the denitration plant are given in Figs 67–69.

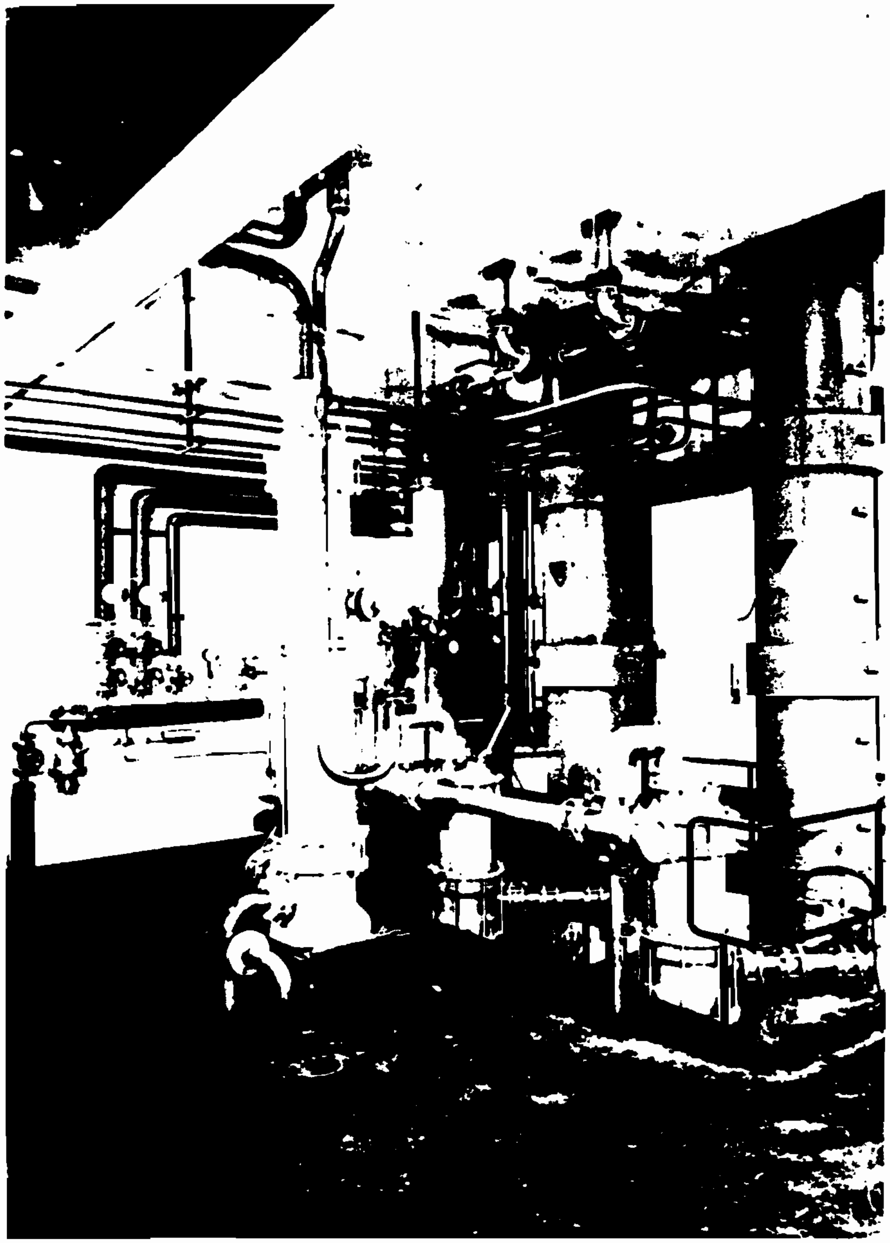


FIG. 67. Denitration of spent acid of glycerine nitration and nitric acid bleaching. (Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

FIG. 68. Denitration of spent acid of NG, NC, NT.
(Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

(B) According to Schott, Mainz [2, 6–8]. The progress of the method of concentrating nitric acid with sulphuric acid was connected with the use of borosilicate glass as a material for the construction plants in combination with tantalum as a heater material to carry out indirect heating of the concentration column [6]. This method of operation was realized by Messrs Schott & Gen., Mainz, who used tantalum heat exchangers on which the acid mixture was sprayed. The exchanger was mounted on the top of the concentration column where the greatest part of the nitric acid is. The heat exchangers are heated by saturated steam and evaporate the major part (*ca*. 90%) of the nitric acid contained in the mixture. Figures 70–72 give general views of some parts of the equipment. An important feature was the introduction of standardized dimensions which make possible the exchange of some parts of the equipment.

3. Re-use of Spent Acid from the Nitration of Glycine

Biazzi S.A. [5] is using an ingenious method of utilizing spent acid from the nitration of glycerine to nitrate toluene to dinitrotoluene. Toluene is added to the spent acid at a temperature gradually increasing up to 90°C. Nitroglycerine

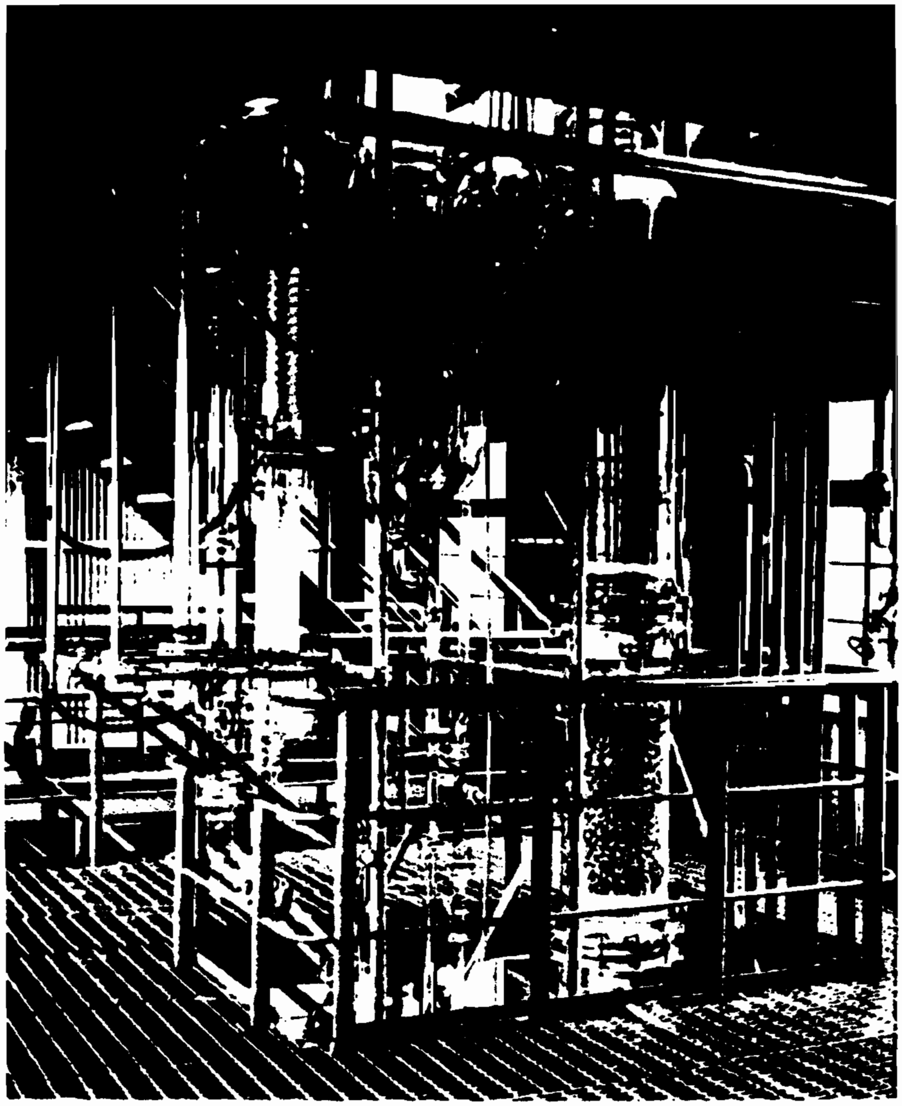


FIG. 69. Denitration and concentration of HNO_3.
(Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)

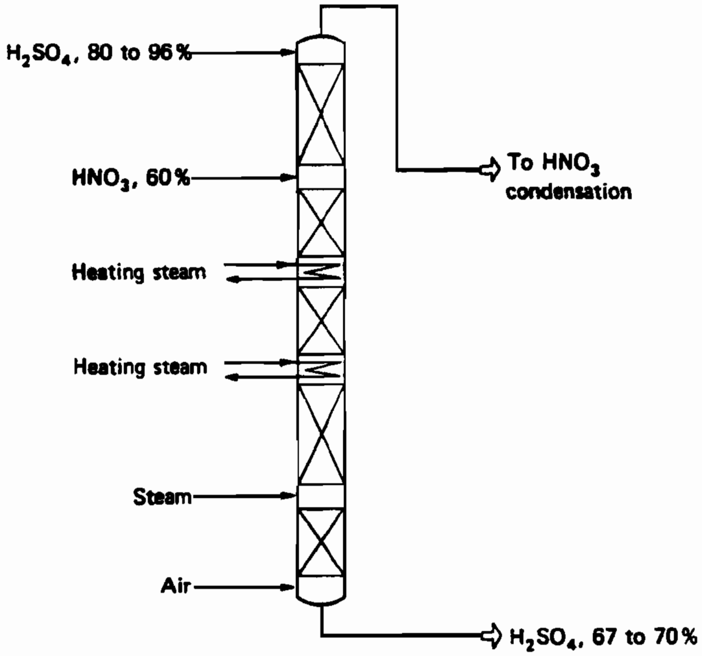


FIG. 70a. Concentration column. (Courtesy Schott & Gen., D-6500 Mainz.)

dissolved in the acid is decomposed and increases the concentration of nitric acid and thus participates in the nitration.

The economy of this method is based on the fact that no denitration plant is needed.

Spent Acid of PETN

The main problem of spent acid after the nitration of pentaerythritol is the instability of the spent acid. Several 'fume off' accidents of spent acid have occurred on its storage after the separation of PETN. Systematic study of the stability of spent acid was carried out by Ramaswamy and Subba Rao [9]. They found that the concentration of 75–80% HNO_3 made the nitric acid unstable due to the presence of organic compounds which can readily be subjected to oxidation. According to the above authors the oxidizing properties of nitric acid predominate at the critical concentration of 75–80%.

Ramaswamy and Subba Rao suggested two methods of stabilizing the spent acid of PETN manufacture.

(1) In the first method live steam of low pressure was injected gradually to keep the temperature at 70 ± 2°C. The injection was stopped when no further

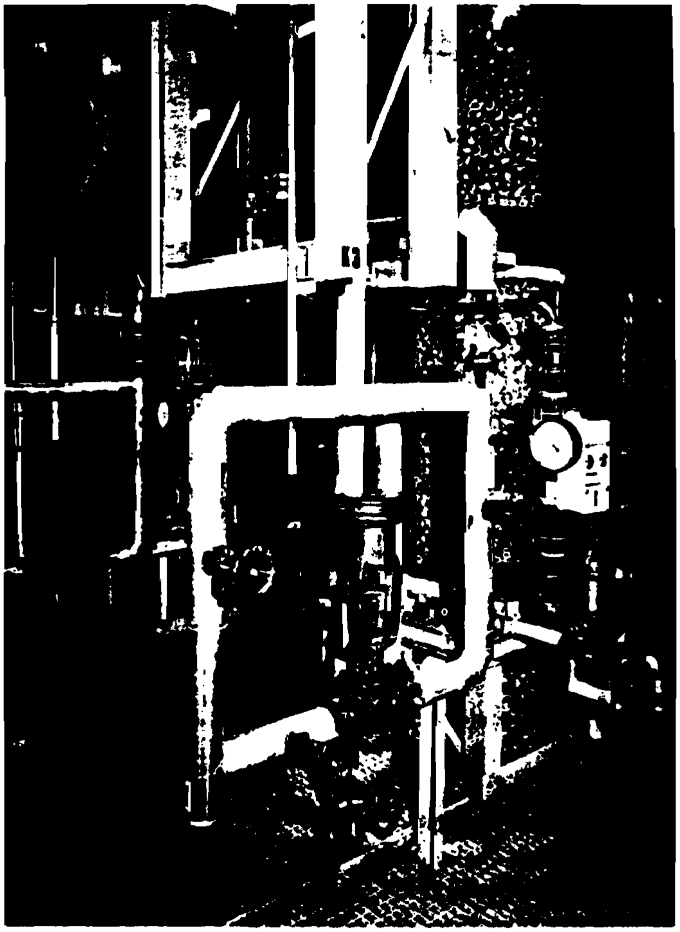


FIG. 70b. Concentration column. (Courtesy Schott & Gen., D-6500 Mainz.)

exothermic reaction was noticed. The concentration of the spent acid falls from 82 ± 2% to 72 ± 2% HNO_3, thus below the dangerous concentration.

(2) In the second method the spent acid was treated with steam so that its temperature was raised to 95–100°C. A highly exothermic and vigorous reaction was accompanied by an evolution of brown fumes and stirring was necessary by blowing in nitrogen or air. The reaction was facilitated by the presence of nitrous acid. The higher the concentration of HNO_2 the lower the temperature of the reaction.

In the normal process of PETN production the content of nitrous acid and organic by-products is below 0.2% and 0.3–0.4% respectively. Ramaswamy and

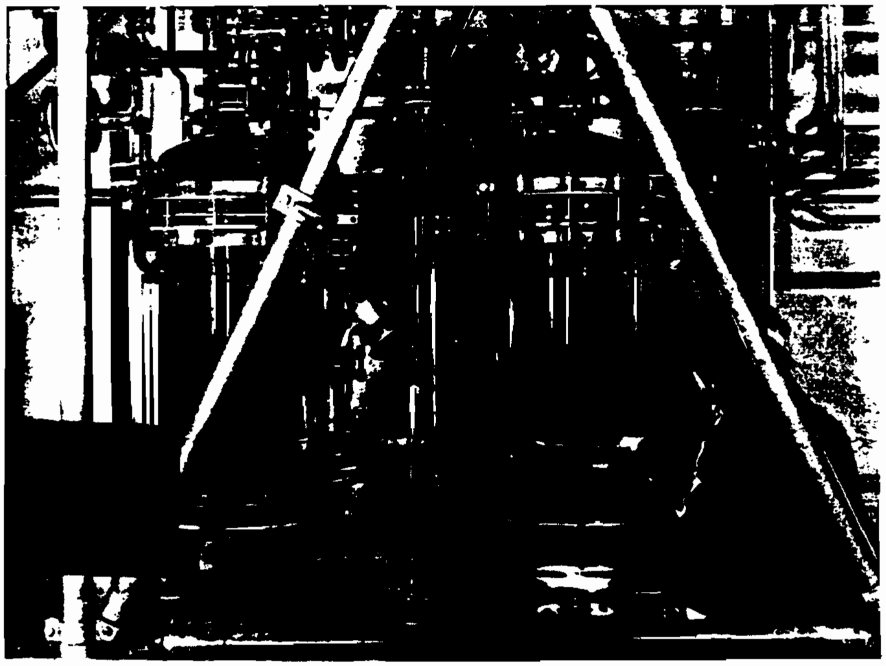


FIG. 71. Heat Exchanger made of standardized parts.
(Courtesy: Schott & Gen., D-6500 Mainz.)

Subba Rao pointed out the ease of hydrolytic reactions in the spent acid, followed by oxidation. They found formic, oxalic and mesoxalic acid among the decomposition products.

Attention should be drawn to the statement by Camera [10] that PETN can be hydrolysed to tri and di-nitrate by nitric acid of 70–90% HNO_3 at 20 and 40°C (see also Chapter X, ref. 149). The unsymmetrically substituted pentaerythritols are particularly apt to vigorous reactions [11].

Plinke [1] described the process of stabilizing spent acid of PETN which, according to the same author contains 80% HNO_3 and 0.1–0.3% organic substances. The spent acid is distilled in a circulation evaporator to completely destroy organic substances and to obtain pure nitric acid. To reach the full decomposition of organic impurities, sulphuric acid of 70% H_2SO_4 is present in the evaporator and remains there to the end of the operation.

Figure 73 is a diagram of the stabilization of residuary nitric acid of PETN according to Plinke. Spent acid from (1) is pumped (4) to evaporator column (3) after being heated at (6). Hot sulphuric acid (70%) flowing from column (3) is cooled at (7) and recirculates to (3). Nitric acid distils from column (3), is cooled through a condenser (8), collected in tank (2) and pumped out through (5). This is nitric acid of 75–80% HNO_3. Nitrous gases escape between (8) and (2).

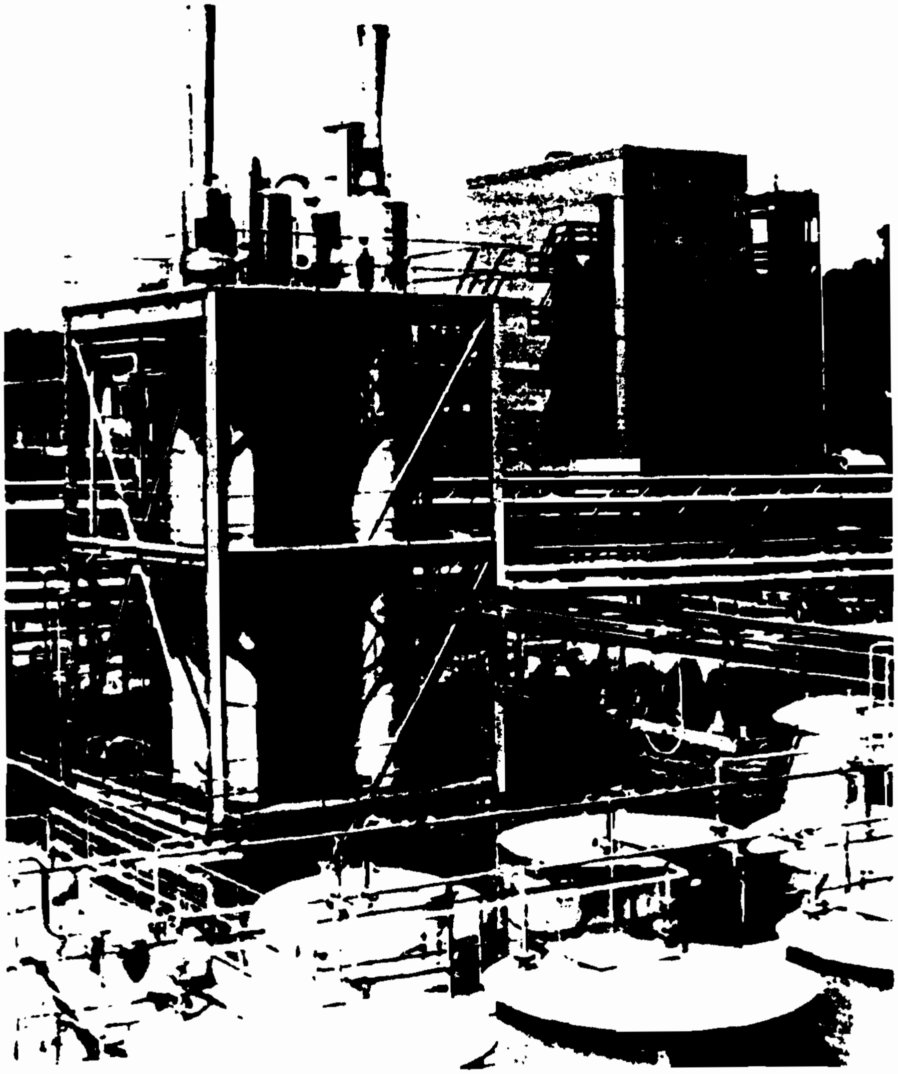
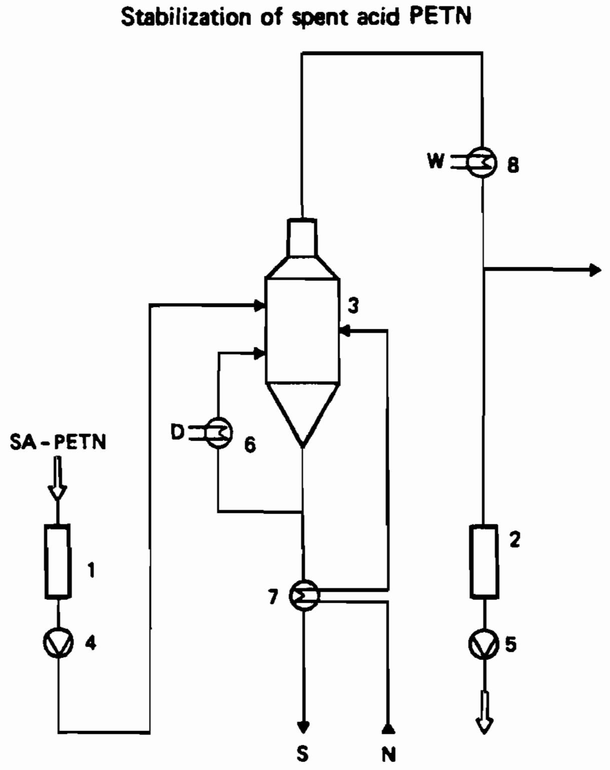


FIG. 72. General View, nitrous fumes absorption.
(Courtesy 'Adolf Plinke Söhne', D-6380 Bad Homburg.)



1 Tank for SA - PETN
2 Tank for N 75 - 80%
3 Evaporator column
4 Pump for SA - PETN
5 Pump for N 75 - 80%
6 Heater for evaporation
7 Heat exchanger for cooling S
8 Heat exchanger for cooling N 75–80%

D = Steam
W = Water

FIG. 73. Stabilization of spent acid of PETN.
(Courtesy, H. Plinke [1].)

Spent Acid from Cyclonite (RDX) Manufacture
(Vol. III, pp. 93, 98–102)

As described in Vol. III Cyclonite can be made by nitrating hexamine (hexamethylenetetramine) with nitric acid. The product is precipitated by pouring the solution into hot water in such a way that the concentration of the acid became 50–55% HNO_3 and the temperature 70–90°C was maintained. All unstable products were decomposed and NO_2 was evolved. This was a 'degassing process'.

A diagram of the concentration of spent acid obtained in that way was given by Plinke [1] Fig. 74. Spent acid from tank (1) enters through heat exchanger

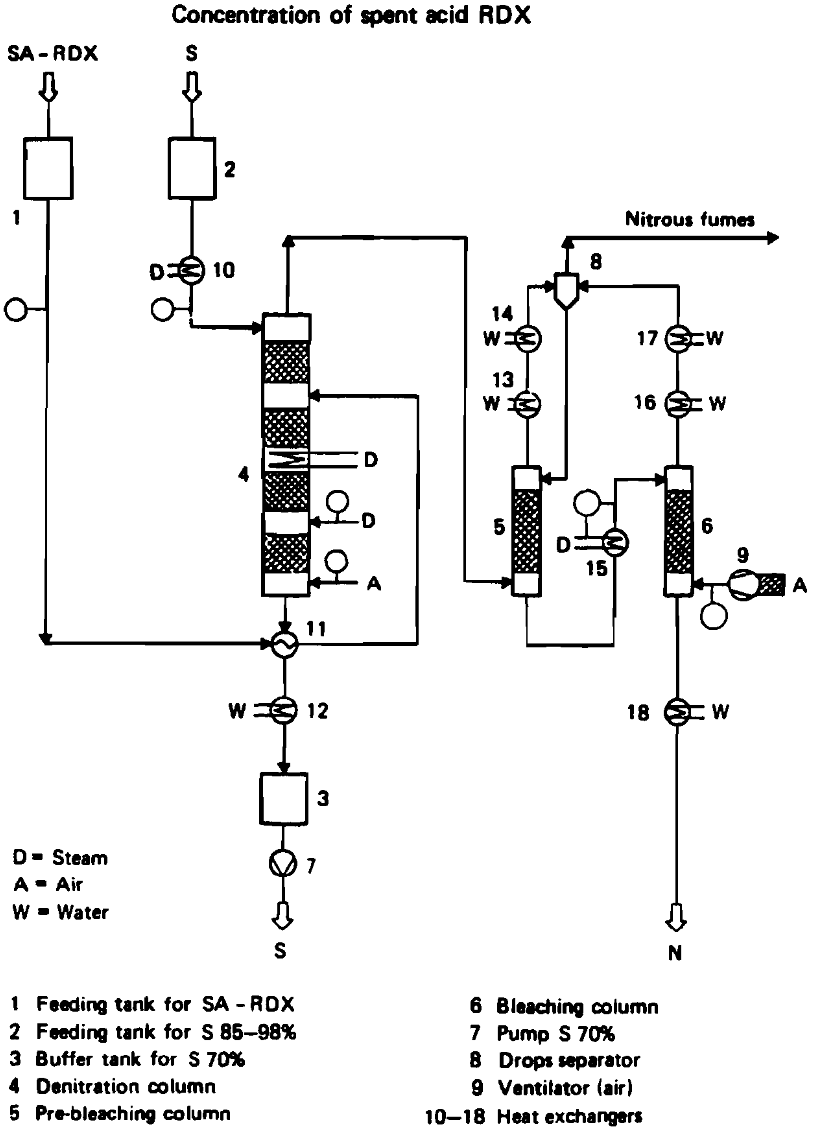


FIG. 74. Concentration of spent acid of Cyclonite (EDX).
(Courtesy H. Plinke [1].)

(11) to the denitration column (4). The column is fed from tank (2) with sulphuric acid (85–95%) pre-heated in (10). The column is supplied with steam and in the lower part – with air. Sulphuric acid (70%) flows down to a buffer tank (3) and through pump (7) to a storage tank. Distilled nitric acid enters the pre-bleaching column (5) and through a dephlegmator (8) to bleaching column (6). Air is blown to the bottom of the bleaching column (6) to help in evacuat-

ing nitrous fumes through (8). A series of heat exchangers (12–17) maintain the correct temperature for the whole system. Nitric acid (98%) leaves column (6) through cooler (18) to a storage tank.

Spent Acid from Nitrocellulose (Vol. II, p. 374)

Plinke [1] gives the average composition of spent acid from the nitration of cellulose: 22% HNO_3, 62% H_2SO_4, 15.8% H_2O, 0.2% nitrocellulose. Highly concentrated nitric acid can be distilled from such an acid without adding sulphuric acid. If sulphuric acid (85–86%) is added, the process is similar to that described in Fig. 74.

This operation is seldom performed and the usual procedure consists in adding concentrated nitric and sulphuric acid to the spent acid.

Spend Acid from TNT

It is very seldom that spent acid from TNT is subjected to distillation. If so, only dilute nitric acid can be obtained according to Plinke [1]. A higher concentration of nitric acid (over 50% HNO_3) can result only after adding concentrated sulphuric and nitric acid. The apparatus is much the same as with the following.

Spent Acid from Mononitration of Toluene

It has been pointed out by Dębowski and Ziółko [12] that the spent acid from mononitration of toluene should not be reused for dinitration by adding nitric and sulphuric acids. It contains 0.3–0.5% mononitrotoluenes and while adding concentrated nitric and sulphuric acids, further nitration of mononitrotoluene present can be produced but requires special precautions.

The authors suggested a simple method of dealing with the spent acid. They extracted the nitro compounds with toluene at 30°C and thus were formed:

(1) toluene with a small proportion of nitro compounds,
(2) spent acid free of nitro compounds.

Toluene (1) can be used for nitration, and (2) spent acid can be safely mixed with concentrated nitric acid and 20% oleum and re-used for mononitration of toluene.

ENVIRONMENTAL PROBLEMS OF DENITRATION

The denitration of spent acids offers some environmental problems. The major one being the escape of nitrous fumes from the denitration columns. According to Berkman [13] they can be introduced to a solution of sodium hydroxide to obtain sodium nitrate and nitrate aqueous solution. The same monograph describes the method of absorption with water [14]. It also gives a description of the industrial method by Andrew and Hanson [15].

An original method was proposed by Kulin and Tikhonenko [16]. They suggested the reduction of nitrogen oxides escaping from the denitration column with methane, for example:

$$CH_4 + 2\,NO_2 \longrightarrow N_2 + CO_2 + 2H_2O$$

$$CH_4 + 4\,NO \longrightarrow 2N_2 + CO_2 + 2H_2O.$$

The reaction can be catalysed by Ni and Cr at 500–600°C and helped by adding some air-oxygen.

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CHAPTER 16

SALTS OF NITRIC ACID

(Vol. II, p. 450)

AND OF OXY-ACIDS OF CHLORINE

(Vol. II, p. 476)

AMMONIUM NITRATE

As is well known ammonium nitrate is the most popular oxygen carrier in explosive mixtures which is also widely used as a fertilizer. Subsequently there is voluminous literature on the properties of ammonium nitrate. Among the greatest problems is its caking. It continues to raise interest and an excellent review has appeared recently [1].

Hygroscopicity of ammonium nitrate was considered to be the major cause of caking [2–5] but later the polymorphism of crystals of ammonium nitrate (IV ⇌ III, Vol. II, pp. 450–452) was recognized as an important factor [6–8]. Particular attention should be paid to the work of Sjölin [8] who studied the phenomenon of caking using X-ray and scanning electron microscopy. His conclusions are summarized as follows: caking is mainly caused by the phase transitions IV ⇌ III at 32°C and depends on dissolution and recrystallization of the solid at the phase transition. If no pressure is applied to the sample a porous powder is formed due to volume increase [14], if pressure is applied, it will result in large crystal surfaces and the dissolution–recrystallization process gives a hard product.

Shneerson *et al.* [7] drew attention to the fact that transition IV ⟶ III does not cause caking while the phase transition III ⟶ IV is of great importance and should be regarded as essential in the process of hardening. Thus hardening occurs during the process of cooling ammonium nitrate heated above 32°C.

Some substances have a great influence on the change IV ⟶ III. Particularly important is the role of water promoting the change [9–13]. Thus it has been shown by Brown and McLaren [10], Wolf and Scharre [11] that ammonium nitrate chemically pure and free of water requires a higher temperature for the transformation of form IV and at *ca.* 50°C it is directly transformed into form

II, whereas a trace of water favours the normal transformation IV ⟶ III at 32°C.

The above mentioned volume increase was described in the important paper by Hendricks *et al.* [14] and in Vol. II (p. 452, Table 110).

As the result of repeated transitions IV ⇌ III breakdown may occur of crystals or prills yielding fine particles which are readily caking through the absorption loss of moisture.

The paper by Thompson [15] should be mentioned as pointing out the importance of the capillary adhesion which can be the major factor responsible for the caking phenomenon narrow layer of the saturated solution between the particles shows a lowered meniscus of the solution, i.e. reduced pressure. Consequently the action of atmospheric pressure becomes sufficiently strong to compress the neighbouring granules into a solid block.

It can be seen from the above discussion that the phenomenon of caking is very complicated with several factors involved in it and there is practically no sufficiently simple explanation of the phenomenon. Subsequently no simple practical solution exists for preventing the phenomenon of caking ammonium nitrate and only a partial solution is known.

Some existing practical methods were mentioned in Vol. II, pp. 453–454. A more systematic description is given below:

1. Covering particles of ammonium nitrate with non-hygroscopic layers of polymers, such as polyvinyl compounds. This however should be limited to substances which could not produce harmful influence on the explosive properties of ammonium nitrate and (for underground work) would not give harmful products after detonation, such as chlorine compounds from polyvinyl chloride.

These conditions are fulfilled with paraffin wax or fuel oil if such an ammonium nitrate is used in explosive mixtures where the above substances are included in the formulation of the explosives. As pointed out in Vol. II (pp. 461–2) small amounts of organic substances increase the ease of detonation of ammonium nitrate and danger of shipping.

2. Non-reactive mineral compounds, such as kaoline in powder form in proportion 2.5% [4]. Carbonates should not be advised as they can react with ammonium salts to form unstable ammonium carbonate. Also silicates are not advised as they can produce silicium oxide which is dangerous in underground work as a cause of silicosis.

3. Salts of stearic acid, such as calcium stearate.

4. Addition of anhydrous salts readily forming hydrates, such as anhydrous: $Mg(NO_3)_2$ (1%) and $Al_2(SO_4)_3$ (2%) [8]. In some patents anhydrous sulphates have been claimed.

Among the agents preventing the transformation of crystalline forms three methods are of great importance (in addition to keeping the ammonium nitrate dry):

1. Introduction of some cations which could enter the crystalline lattice, such

as K^+ which has an ionic radius (1.33Å) of the same order as NH_4^+ (1.43Å). The presence of 3–4% KNO_3 suffices to stabilize form III (Vol. II, pp. 454–5).

2. Introduction of some mineral substances. Among the minerals kaoline or kieselguhr in quantity 2.5% were suggested [4]. Brown, Green and Blanton [16] recommended adding a mixture of boric acid, diammonium phosphate and ammonium sulphate in quantity of less than 0.5%. They suggested a composition containing 0.2% H_3BO_3, 0.2% $(NH_4)_2HPO_4$ and 0.01% $(NH_4)_2SO_4$. Prills of unprecedented hardness resulted, completely stable over 32°C transitions. The authors found this mixture much superior to previously used kaoline or kieselguhr. Engel [17] found that the volume increase due to the phase transitions IV $\rightleftharpoons$ III at 32°C was reduced by incorporating diammine complexes of Ni and Cu into the lattice. The transition temperature raised above 50°C. The effect of complexes of Zn was less marked.

Glazkova in her monograph [18] described water resistant ammonium nitrate 'Zh V' containing 0.07–0.10% 'iron sulphate' and 0.3–0.4% of an undisclosed hydrophobic component.

3. Addition of surface active agents, such as triphenylmethane dyestuffs, can prevent caking of ammonium nitrate in quantity as low as 0.05% (see Vol. II, p. 454) and [19].

It is now accepted that surface active substances are very helpful as anticaking agents. A review was published on the subject by Kołaczkowski and Biskupski [108]. Sodium alkylarylsulphonates and various substances with trade names were examined in quantity 0.05–0.50%. The authors draw attention to the fact that before the use of such substances experiments should be carried out on the influence of the additives on thermal stability of ammonium nitrate. Some of them appreciably lower the temperature of the decomposition of ammonium nitrate which should not be less than 220–240°C. It should also be borne in mind that the addition of an organic substance or (generally speaking) of a substance which can burn increases the sensitivity of ammonium nitrate to detonation. Small amounts, of the order of 1–4% of organic substances considerably increase the sensitiveness (Vol. II, pp. 461–462 and the description of accidents on p. 441, this volume). Thus the sensitivity to detonation of ammonium nitrate with surface active agents should be examined and mixtures with additives should be handled with precaution as with explosives.

Hygroscopicity of Ammonium Nitrate

The hygroscopicity of ammonium nitrate is its great drawback. The problem occurred particularly with the use of ammonium nitrate mining explosives their storage and use in damp places. The usual method of reducing hygroscopicity consists in incorporating small proportions of calcium, zinc and iron salts of fatty acids, usually stearic acid.

Silicon resins can also be used (Vol. III, p. 421). The problem of the hygroscopicity of ammonium nitrate is discussed in Chapter XIX on Mining Explosives.

Chemical and Explosive Properties

Andreev and Glazkova [20] carried out pioneering work on the action of various substances on the rate of burning ammonium nitrate. In their later paper [21] they examined the influence of the addition of various salts to ammonium nitrate on its rate of burning – Table 71.

TABLE 71. Rate of burning of ammonium nitrate in a closed vessel. Density of the samples 1.6–1.7 g/cm^3 [21]

Addition of 10%	Mean pressure atm	Mean rate of burning g/cm^3, sec.	Relative rate of burning
Pure NH_4NO_3	190	0.53	100
NaCl	357	1.43	270
KCl	335	1.27	240
K_2Cr_2	363	1.47	270
$K_2Cr_2O_7$	292	1.17	220
$BaCl_2$	322	1.57	290

Obviously the rates of burning are also influenced by different pressures in the closed vessel and therefore the figures cannot be taken as strictly comparable. Nevertheless higher rates of burning of mixtures containing barium chloride, potassium bichromate and sodium chloride are evident.

According to Rosser, Inami and Wise [74] ammonium bichromate, soluble in molten ammonium nitrate, was found to be a catalyst of the decomposition of ammonium nitrate at temperatures 460–520 K. For low concentration of the catalyst the principal products of decomposition were N_2, N_2O, H_2O, HNO_3. The catalysed decomposition was inhibited by ammonia and water, promoted by nitric acid.

The finding of Andreev and Glazkova [21] is interesting in that ammonium nitrate containing potassium bichromate can burn faster by adding potassium and ammonium oxalate, under low pressure (3 atm), but under higher pressure of the order of 300–400 atm. the presence of oxalates reduces the rate of burning.

The problem of burning ammonium nitrate and its mixtures is widely described in the excellent monograph by Glazkova [18]. The problem is not only of great theoretical but also of practical importance. It is connected with the use of ammonium nitrate explosives in coal-mines and their ability to burn which creates an additional danger of their use. In the present book it is discussed in Chapter XIX on Mining Explosives.

Some organic substances (e.g. cellulose) lower the thermal stability of ammonium nitrate. According to Findlay and Rosebourne [22] an ammonium nitrate–paper combination was shown to self heat at the temperature range used in bagging and shipping the fertilizer grade of NH_4NO_3, so that it often arrived at a sea-port appreciably hotter than when it was bagged (90 ± 20°C). Bag imprittlement and even charring by self-heating caused excessive spillage, contamination and required rebagging. Several spontaneous fires in rail trucks were recorded, preceding the Texas City catastrophe [23]. Immediately after the Texas City catastrophe the paraffin-wax coating of ammonium nitrate was replaced by kieselguhr – an inferior but much safer anticaking agent. Kieselguhr coated ammonium nitrate (fertilizer grade) was widely in use for AN/FO explosive mixtures [23].

A detonation of 80 tons of ammonium nitrate in plastic bags occurred in 1978 at Manouba in Tunisia [39]. The floor of the store house was covered with saw dust for the purpose of absorbing any liquid from broken bags. It was stated that saw dust mixed with oxidizing substances in the presence of moisture can undergo fermentation causing a temperature rise and ignition of ammonium nitrate. Prior to the detonation red fumes came from the store house, which indicated the beginning of the decomposition which ended in detonation.

HYDRAZINE NITRATES (Vol. II, p. 464)

Two hydrazine (or hydrazinium) nitrates are known: mono- and dinitrate.

Hydrazine Mononitrate

Mononitrate $NH_2\overset{+}{N}H_3\overline{N}O_3$ exists in two forms: α and β. α-Form is stable and has m.p. 70.7°C, β-form is unstable, has m.p. 62.1°C [24]. β-Form is obtained by keeping the substance at 110°C for 30 min and cooling slowly to 61°C. The crystal structure was examined, and so were refractive indexes of α and β-forms: 1.065 and 1.458 respectively [25]. If a concentrated solution of β-form is cooled from 100°C down to room temperature α-form was separated [26]. The transformation enthalpy ΔH of form β to α is 2.0 kcal/mol [27]. Thermal decomposition was studied by a number of authors. At 100°C the evolution of ammonia is less prominent than that of ammonium nitrate: 0.005% as compared with 0.016% [28]. Shidlovskii and co-workers [29] found that the decomposition started at 180°C, increased above 240°C and became explosive at 270°C. The 'Bruceton up- and down-down' method (Vol. III, p. 445) gave 50% probability of ignition at 307°C [27]. Decomposition to 200–300°C under 1 atm. resulted in decomposition according to equation [30]:

$$4\,N_2H_4\cdot HNO_3 \longrightarrow 2\,NO + 5\,N_2 + 10\,H_2O. \tag{1}$$

Decomposition *in vacuo* was investigated by Breisacher and co-workers [31].

When ignited, hydrazine nitrate burns very readily, the flame is extinguished upon removal of the ignition source. Shidlovskii *et al.* [29] found that the addition of 10% $K_2Cr_2O_7$ assures steady burning.

Thermochemical and some explosive data were collected by R. Meyer [32]:

enthalpy of formation	—620.7 kcal/kg
heat of explosion	924 kcal/kg
volume of gases	1001 l/kg
oxygen balance	+8.6%
density	1.64 g/cm^3
decomposition temperature	229°C.

High lead block test (408 cm^3) and velocity of detonation (8690 m/s) were given.

The high figures of the velocity of detonation and of lead block aroused much interest in the compound and have been reported by several authors.

Thus explosive properties were reported by H. K. James *et al.* [27]: the rate of detonation of molten hydrazine nitrate 75°C was found to be 8500 m/s, and ballistic mortar 120.4 ± 0.5 (picric acid = 100) or 142 (TNT = 100).

Some other authors also reported [32] high velocity of detonation: 8500–8510 m/s with cartridges of 6.4 cm diameter, pressed to density 1.59–1.6. Price [33] found that the infinite charge diameter detonation velocity can be expressed by the equation $D = 5390\ (\rho\ HN \cdot 100)$ where $\rho\ HN$ is the density in g/cm^3. Kurbangalina and Tinokhin [34] found that the critical diameter increases with an increase of water content and the rate of detonation can vary from 2000 to 8000 m/s.

Meyer [32] reported that mixtures of hydrazine nitrate with HMX (Octogen) pressed to high density can be over 9000 m/s.

Attention should be drawn to two monographs on hydrazine: [26] and [30].

Hydrazine Dinitrate

(Vol. II, p. 465)

Hydrazine dinitrate $NH_2NH_2(HNO_3)_2$ was described by Sabanejeff [35]. It is a substance which decomposed at *ca.* 80°C. When heated rapidly it melts at 103–104°C. It can be obtained by neutralizing hydrazine hydrate with two moles of nitric acid or by acting barium nitrate on hydrazine sulphate [26], [30]. It decomposed on steam bath or on standing at room temperature over sulphuric acid with the evolution of hydrazoic acid [35].

It is an explosive which is stronger, but less sensitive to impact, than Tetryl but weaker than PETN [33]. However owing to its low stability it is of little practical value.

Hydrazine Nitrate Complexes ('Hydrazinates')

Salts of bivalent metals (Ni, Co, Zn, Cd and Mn) form complexes with hydrazine nitrate of a general formula

$$\underset{\text{I}}{[M(N_2H_4)_2]\,(NO_3)_2} \quad \text{and} \quad \underset{\text{II}}{[M(N_2H_4)_3]\,(NO_3)_2}.$$

For the first time Ni salts (II) were obtained by Franzen and Meyer [36] and a number of them were prepared by Médard and Barlot [37]. According to the latter authors some of hydrazinatés possess initiating properties and are described in Chapter XVII on initiating explosives.

METHYLAMINE NITRATE (Vol. II, p. 465)

Methylamine nitrate (m.p. 111°C) recently gained much significance as an important ingredient of 'slurry' explosives because of its greater aptitude to detonation than that of ammonium nitrate. More data on explosive properties were recently given by R. Meyer [32]:

enthalpy of formation	−896 kcal/kg
heat of explosion	887 kcal/kg (the given figure formerly – 1200 kcal/kg – Vol. II, p. 466 – should be corrected as being too high).
Volume of gases	1027 l/kg,
density	1.422 g/cm^3.

According to Cottrell and Gill [38] unconfined methylamine nitrate melts and boils (230°C) without decomposition.

With regard to preparation of the compound, apart from the straight forward formation from methylamine and nitric acid (66%) (as described in Vol. II) another method based on the Plöchl reaction, by reacting ammonium nitrate with formaldehyde at 80–100°C, as was suggested by the author of this book [39] and brought to industrial application:

$$NH_4NO_3 + 2\,CH_2O \longrightarrow CH_3NH_3NO_3 + HCOOH. \tag{2}$$

Although laboratory experiments have shown that methylamine nitrate is not very sensitive to impact, it gave a disastrous explosion at Potomac River, W. Virginia in 1976 [40] in two tank cars containing 86% solution of methylamine nitrate. The explosion probably took place due to friction in a pump or to a collision.

TETRAMETHYLAMMONIUM NITRATE $(CH_3)_4\overset{+}{N}\overset{-}{N}O_3$ (Vol. II, p. 466)

This substance was found to be difficult to bring to explosive decomposition.

However the mixtures of tetramethylammonium nitrate with polymers can burn in the presence of ferric oxide which proved to be an efficient catalyst for burning such mixtures [41].

Fe_2O_3 has a similar catalytic effect on the combustion of guanidine nitrate.

GUANIDINE NITRATE (Vol. II, p. 466)

Enthalpy of formation of guanidine nitrate was determined by Krivtsov, Titova and Rosolovskii [105]. It was found to be $-\Delta H_f = 93.0$ kcal/mol.

NITRATES OF AROMATIC AMINES

A number of nitrates of aromatic amines were recently described [42]. No information on their explosive or burning properties is available.

AMMONIUM CHLORATE (Vol. II, p. 476)

This substance has no practical application owing to its low stability, but it was important to study conditions influencing the decomposition and possibly the mechanism of decomposition. The early papers [43, 44] gave only a general description of the decomposition of the substance. A much more detailed account was given by Solymosi and Bánsági [45]. They studied the decomposition by measuring the pressure of non-condensable gases and the loss of weight at different temperatures. A measurable decomposition started at 50°C, but some days after the preparation of the substance according to (3),

$$NH_4Cl + NaClO_3 \longrightarrow NH_4ClO_3 + NaCl \qquad (3)$$

a slight decomposition was observed even at -5°C. The explosion of freshly prepared substance occurred at 90°C. The activation energy was calculated as being 22–25 kcal/mol. The addition of ammonia stabilized the substance, but the addition of chloric acid considerably increased the rate of decomposition.

Attention should be paid to the fact, that the substance is dangerous and all possible reactions leading to the formation of ammonium chlorate should be carefully avoided.

AMMONIUM PERCHLORATE (Vol. II, p. 477)

An enormous amount of work has been done in the last 30 years on ammonium perchlorate (AP). Originally it was reflected in the monograph by Schumacher [46] (Vol. II, p. 477) and more recently – the excellent review by Jacobs and Whitehead has appeared [47]. It contains all the important information available up to 1968. The pertinent data will be repeated in the present book to obtain a full picture of this compound and some more recent descriptions will be given here. Also the monograph of Glazkova [18] on catalytic decomposition should be mentioned.

Crystal Structure and Physical Properties

Two crystal structures of ammonium perchlorate are known: the lower-temperature orthorhombic form existing below 240°C and cubic form above that temperature [48]. The density of orthorhombic and cubic forms is 1.95 and 1.76 g/cm^3 respectively [47]. Ammonium ion undergoes an almost free rotation with the potential barrier of 0.55 ± 0.05 kcal/mol [49]. The heat of transition from orthorhombic to cubic system is accompanied by a heat effect of 2.3 ± 0.2 kcal/mol [50, 110]. AP is nonhygroscopic [81].

The specific heat of ammonium perchlorate [51] is 0.309 cal g^{-1} deg^{-1} between 15 and 240°C and 0.365 cal g^{-1} deg^{-1} above 240°C. The electrical conductivity was also examined [52–54]. The activation energy of electrical conductivity changed from 45 kcal/mol at high temperature (over 255°C) to 4 kcal/mol below 92°C.

Thermal Decomposition and Burning of AP

General information. Ammonium perchlorate (AP) is stable at room temperature. It begins to decompose above 130°C [56] or 150°C [55]. According to Andreev and Sun Tsuan-tsai [55] at 160°C half-life of AP is 25,000 min and at 270°C is 225 min (for comparison they gave the half-life figures for nitrocellulose at 160°C and for TNT at 270°C: 170 min and 20 min respectively). Thus the decomposition of AP is much slower than both above mentioned explosives. The decomposition of ammonium nitrate above 170°C (i.e. above its m.p. which is 169°C) is much faster than that of AP due to the fact that AP does not melt. Thus the half-life of ammonium nitrate at 286°C and of ammonium perchlorate at 280°C is 5 min and 170 min respectively.

The decomposition of AP with temperature follows an S-curve, which is typical for autocatalytic reactions. Thus, there is an initial increase in the rate of decomposition through the formation of the products of decomposition and the fall of the rate after these products were subjected to decomposition. The formation of an unusual product at lower temperatures (220–300°C) has already been described in Vol. II, p. 479. Above 350°C the reaction is no more autocatalytic.

Numerous products are formed during the decomposition of AP. They were examined in Dodé's pioneering work [56] and confirmed by Bircumshaw and Newman (Vol. II, p. 478). Further experiments were carried out by Rosser, Inami and Wise [57]. Dodé identified the products such as chlorine dioxide (at temperatures below 300°C), nitrogen, water, oxygen, nitrous oxide, hydrogen chloride, nitrosyl chloride, nitrogen trioxide and nitrogen dioxide, the latter three compounds being the result of the secondary reaction of nitric oxide with chlorine and oxygen.

Wise *et al.* [57] gave a quantitative summary of the products of decomposition between 250° and 325°C, for example at 275°C they found:

0.50	O_2	
0.047	N_2	
0.35	N_2O	
0.39	Cl_2	Moles per mole of decomposed AP
0.19	HNO_3	
0.16	HCl	
0.019	NO	

The authors tried to rationalize the reaction in terms of a decomposition equation beginning by electron transfer followed by proton transfer (4):

$$NH_4ClO_4 \longrightarrow NH_4^+ + ClO_4^- \longrightarrow NH_3 + HClO_4. \tag{4}$$

The proton transfer was earlier suggested by Davies, Jacobs and Russell-Jones [82]. A number of Soviet authors – Boldyrev *et al.* [118] confirmed the mechanism of proton transfer. According to Pearson and Sutton [75] perchloric acid decomposed to yield ClO_3 and ClO which were detected in fragmentation in a mass spectrometer.

It appears that the reaction of decomposition of AP is too complicated to be presented in one equation. Nevertheless the deflagration of AP starting at *ca.* 450°C can be depicted by equation (5) according to Kaye [81]:

$$4\,NH_4ClO_4 \longrightarrow 2\,Cl_2 + 8\,H_2O + 2\,N_2O + 3\,O_2. \tag{5}$$

Another equation for the decomposition of AP is (6) [47]:

$$2\,NH_4ClO_4 \longrightarrow Cl_2 + 4H_2O + 2NO + O_2. \tag{6}$$

Probably both reactions can run simultaneously.

A phenomenon of sublimation of ammonium perchlorate occurred simultaneously with decomposition as mentioned previously (Bircumshaw and Newman, Vol. II, p. 478), and suggested by Dodé [58], Jacobs and Powling [59] and made the process still more complicated.

The activation energy of thermal decomposition of AP varies from 17 to 40 kcal/mol according to various authors [47]. The wide discrepancy between their results was due to various conditions of the reactions, various techniques used and is a sign of the complicated nature of the reactions of the decomposition of AP.

Mass spectrometry fragmentation was investigated by a number of authors [60] (also references in [47]). More recent work was done by Volk and Schubert [61]. At 240° and 280°C they found the fragments: NH^+, NH_2^+, NH_3^+, H_2O^+, NO^+, O_2^+, Cl^+, N_2O^+, NO_2^+, ClO^+, ClO_2^+, ClO_3^+, $HClO_4^+$ m/e.

Thermal Decomposition of Irradiated Ammonium Perchlorate

(Vol. II, p. 481)

The work of Freeman and Anderson [62] was continued and confirmed the previous observation. Irradiation increases the number of nuclei and this affects the decomposition of the substance: the decrease in the induction period and an increase in the rate constant [63a]. A detailed kinetic study of pre-irradiation was made by Harley and Levy [63b]. They also found that the activation energy of thermal decomposition of AP was unchanged by irradiation at 28.4 ± 2.5 kcal/mol.

Influence of Pressure on Burning of AP

Ammonium perchlorate can burn on condition that it is confined and that the pressure inside the vessel is a minimum of 45 atm. [64], or according to other authors above 20 atm. [65]. The size of crystals of AP have a decisive influence on this limit of pressure. Thus it was found that very fine substance (UFAP = ultra fine AP) can burn in the open under atmospheric pressure [81]. A number of authors examined the deflagration of ammonium perchlorate at different temperatures and pressures: Watt and Patterson [119], Boggs and co-workers [67], Glazkova [66, 18]. Glazkova examined the influence of pressures as high as 1000 atm.

All authors drew attention to a number of factors influencing the data referred to burning AP such as: size of crystals, density, confinement (e.g. diameter of tubes), material of the tubes (e.g. glass, Plexiglas). The typical shape of curves: rate of burning/pressure is presented in Fig. 75 according to Glazkova [18]. The region below 300 atm. is depicted in Fig. 76 [67], and merits special attention. Here the analysis will be given as presented by Glazkova [66].

Four regions of burning should be distinguished, viz:

(I) From 20 to *ca.* 55 atm. A steady increase is marked in the rate of burning. The exponent n in the formula of burning $u = b \cdot p^n$ is *ca.* 0.77 according to [68].

(u – is the rate of burning in g/cm^2 sec, b – a coefficient, p – pressure).

(II) From *ca.* 55 to 150 atm. the slope du/dp is smaller, and the exponent n has a lesser value than in (I), for example 0.55.

Both regions were described by Glazkova as those of steady burning.

(III) From 150 to 300 atm. The burning is characterized by a rapid fall in the rate of burning with an increase of pressure [67]. The exponent n can acquire a negative value, for example −3.8. In some experiments Glazkova observed a plateau in this region of pressures. A plateau was also found by Manelis and Strunin [69].

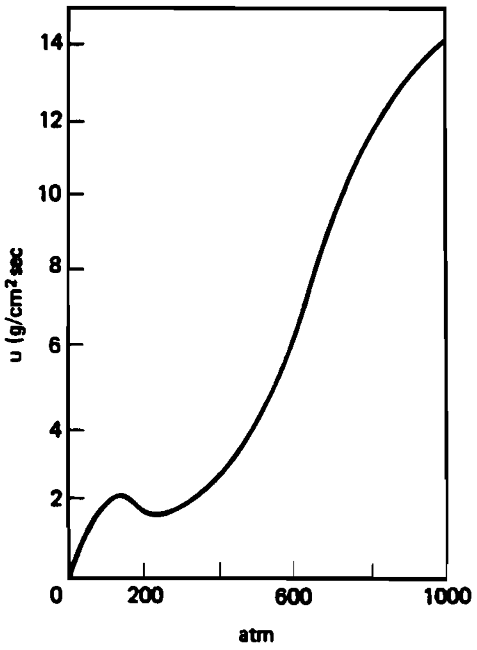

FIG. 75. Rate of burning against pressure of ammonium perchlorate, according to Glazkova [18].

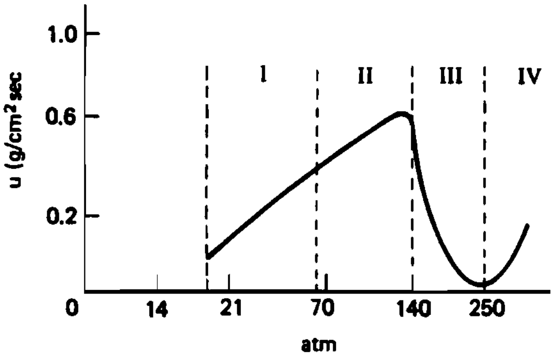

FIG. 76. Rate of burning of ammonium perchlorate below 300 atm. according to Boggs *et al.* [67].

(IV) From pressure over 300 atm. an increase is observed in the rate of burning which is particularly marked over 500 atm. The exponent *n* acquires a value $n > 1$.

Burning between 150 and 300 atm. (and according to Glazkova up to 500 atm.) is pulsing and unstable. Glazkova and Bobolev [70] rationalized it in terms of the formation of water as one of the products of the reaction of decomposition of AP. Water remains on the surface of crystals as a liquid. This follows from the temperature of boiling water under high pressure. This temperature can be higher than that of the surface of solid AP, for example: under 150 atm., the temperature of boiling water is 360°C whereas the surface has a temperature 320°C.

A factor of sublimation should also be considered. Guirao and Williams [71] described the deflagration of AP at pressure between 20 and 100 atm. and suggested that a dissociate sublimation process is likely to exist at the interface between the gaseous and condensed phases.

Density and Critical Diameter

Bakhman, Belyaev, Lukashenya and Polikarpov [72] studied the influence of the density of AP on the rate of burning under pressures 5–100 atm. The mass rate of burning increases with the increase of density. Thus confined samples with densities from 1.465 to 1.95 g/cm^3 increased by factor 2.66. Glazkova [66] carried out wide experiments on the influence of density and obtained a somewhat complicated picture: generally the rate of burning increases with density but follows the same rule as regards the influence of the pressure as depicted by Figs 75–76. A pulsing burning was observed under pressures 160–300 atm.

Samples of AP do not burn if they are confined in tubes of a diameter below a certain limit – the critical diameter. This was investigated by Glazkova [73] for the density 1.2–1.4. The smallest critical diameter corresponds to the substance burning under 100–150 atm., that is where the rate of burning is the highest. The maximum critical diameter is at 20 atm. and further increase of the pressure reduces the critical diameter.

It should be borne in mind that the results of different authors are not in complete agreement, due to the complicated nature of burning ammonium perchlorate, which depends on so many factors mentioned already and some other factors such as the size of particles of AP, a kind of confinement. The burning of AP under different pressures indicates that the rocket propellant with AP should not be used in systems where the pressure is over 150 atm. that is, where burning is unsteady (pulsating) and excludes the systems where the pressure is over 300 atm and the exponent $n > 1$.

Decomposition (at higher temperatures) and Burning of Ammonium Perchlorate with Various Additives

A considerable amount of work has been dedicated to the influence of additives on the decomposition of ammonium perchlorate. It started by the pioneering work of Friedman and co-workers [64] who studied the decomposition of ammonium perchlorate under pressure from atmospheric to 340 atm. They found that an addition of *ca.* 3% of some mineral compounds possess a catalytic action. The best catalyst was found to be cupric chromite containing 85% CuO and 15% Cr_2O_3. Ammonium perchlorate with 3% of cupric and chromic oxides begins to burn steadily under pressure over 135 atm. and 230 atm. respectively. With cupric chromite the steady burning was much faster and started under pressure of 100 atm.

The catalysts introduce some change in the composition of the products formed during the burning of AP. The main reactions of the decomposition of NH_4ClO_4, according to Rosser and co-workers [57] consists in the sequence of the reaction already described (4).

The experiments of Rosser, Inami and Wise [57] were the continuation of their work on catalytic decomposition of ammonium nitrate [74]. They examined the action of copper chromite. They found that it acted at the early stage of the reaction and its action disappeared after copper chromite was oxidized by the products of catalytic reaction. Cobalt oxide was found to be an exceptional catalyst: it produced NOCl and NO_2Cl as major products and only a trace quantity of N_2O_3. The authors came to the conclusion that copper chromite catalysed thermal decomposition of AP according to an electron transfer mechanism (4).

Pearson and Sutton [75] did not agree with this view. On the basis of their own experiments and those of other authors [77, 82] that both the catalysed and uncatalysed decomposition of ammonium perchlorate proceeds by proton transfer (4) and (7):

$$NH_4^+ ClO_4^- \longrightarrow NH_3 + HClO_4. \tag{7}$$

An important work was done by Shimagin and Shidlovskii [76]. According to these authors the presence of HCl (equation 6) in the decomposition products is not affected by 5% of Cr_2O_3, MnO_2, Fe_2O_3, NiO, Cu_2O but these oxides suppressed the formation of N_2O and increased the concentration of NO. On the contrary zinc oxide strongly reduced the amount of HCl and did not suppress the formation of N_2O.

Pellett and Saunders [77] studied the action of ruby laser on the AP-catalyst system. The first products evolved were NH_3 and $HClO_4$ and after that the products of their reaction appeared: H_2O, ClO_2, NO, HClO, Cl_2 and NO_2. The decomposition of $HClO_4$ yielded HCl and ClO_2.

Strunin and Manelis [78] made the observation that the thermal decomposition of AP at 230–260°C was not influenced by pressure of 100 atm of an inert gas.

Kaye in *Encyclopedia of Explosives* [81] describes over 30 metal oxides and salts which provide a catalytic effect upon the thermal decomposition of AP. They are oxides of Al, Cd, Cr(II), Cu(I), Cu(II), Fe(III), Mg, Mn(III), Mn(IV), Mn_3O_4, Ni(II), Ni(III), V(V), Zn and chlorides: of the same metals. Also perchlorates of Cd, Cu(II), Hg(II), Mg, Zn possess a catalytic action.

Mechanism of Low-Temperature Decomposition of AP

The microscopic study of the formation and growth of nuclei in solid ammonium perchlorate was studied by a number of authors (Vol. II, p. 481). Raevskii and Manelis [79a] found that the decomposition centres of orthorhombic form consists of a large number of ellipsoid nuclei of 1–2 μm. They are not stationary but moving at the speed of the order 7–10 μm/min at 230°C. Their activation energy is 31 and 33 kcal/mol depending on the direction of the movement.

In the decomposition of the cubic form (above 240°C) they are spherical, randomly distributed throughout the crystals. The activation energy of their growth is 17 ± 1 kcal/mol above the transition point. The dislocation in crystals during their decomposition was revealed by etching the surface of crystals with ethanol [79b].

A number of other works on low-temperature decomposition were subjected to a detailed review [47]. Also the monograph of Glazkova [18] should be consulted.

Explosive Properties of NH_4ClO_4

The following are data according to Meyer [80]:

enthalpy of formation	–602 kcal/kg
heat of explosion	266 kcal/kg
deflagration point	350°C
lead block expansion	195 cm^3

According to Kaye in *Encyclopedia of Explosives* [81]: dry, fine grade AP can detonate from No 8 blasting cap,

detonation rate of dry AP was 3400 m/s,
detonation rate wet with ethanol AP 4200 m/s,
detonation rate wet with acetone AP 4500 m/s,

(no information was given as to the density and the quantity of the liquid).

Lead block test gave 46% of picric acid, ballistic mortar – 100% of TNT.

An electrostatic discharge of over 5 joules was required to initiate a decomposition of AP.

Impact sensitivity was found to be 91 cm for 50% explosion (as compared with 61 cm with picric acid).

Heat Test at 100°C: after 48 hours 1% weight loss, between 48 and 96 hours 0.6% loss. No explosion occurred after 100 hours. The above data indicate a high stability of ammonium perchlorate.

The detonation equation (8) was given by Kaye [81]:

$$2\,NH_4ClO_4 + 4\,H_2O + O_2 + Cl_2 + 2\,NO. \qquad (8)$$

Price, Clairmont and Jaffe [83a] carried out an extensive investigation of detonation of ammonium perchlorate as a function of density and particle size.

They expressed their results in equation (9):

$$D_l = -0.45 + 4.19\,\rho_0 \tag{9}$$

where ρ_0 is the density in g/cm³, D_l = detonation velocity in mm/μs corresponding to the infinite charge diameter.

Equation (9) is valid for $\rho_0 = 1.0\text{–}1.26$.

Price and co-workers [83b] extended their results to densities below 1.0 and their equation took the shape:

$$D_l = 1.146 + 2.576\,\rho_0$$

$$0.55 < \rho_0 < 1.0\ \text{g/cm}^3.$$

For $\rho_0 = 1.0$ the values of D were:

diameter d cm	
2.54	2.824 mm/μs
3.495	3.027
5.08	3.295
7.62	3.393

The extrapolated value D_l was 3.702.

At a still lower density, e.g. $\rho_0 = 0.55$ the D_l value was 2.530 mm/μs.

Decomposition occurred according to the equation

$$NH_4ClO_4 \longrightarrow 0.5\,N_2 + 0.5\,Cl_2 + 2\,H_2O + O_2$$

Manufacture of Ammonium Perchlorate

On a commercial scale AP is prepared by the interaction of ammonium chloride with sodium perchlorate. The less soluble AP precipitates and is filtered off leaving a solution of NaCl. A schematic diagram by Kaye [81] is given in Fig. 77.

According to Schumacher's patent [84] the reaction between anhydrous ammonia, concentrated hydrochloric acid and aqueous (56%) $NaClO_4$ and recycled mother liquor from the NaCl crystallizer are heated with steam to 90°C. By adding HCl the pH of the reaction is kept close to 7.0. The reaction liquor enters a crystallizer where the temperature is lowered to 35°C by vacuum evaporation and brought to a supersaturation. The crystals of AP are centrifuged, recrystallized, washed with a saturated solution of AP (to remove the traces of sodium chloride). The mother liquor enters the sodium chloride crystallizer where water is removed by vacuum evaporation and the mother liquor is recycled to the reactor.

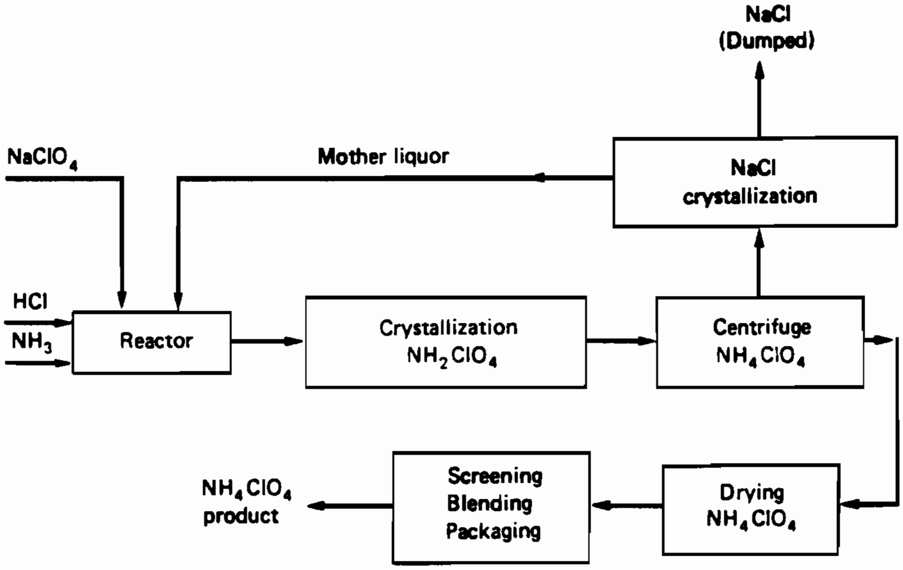

FIG. 77. Diagram of manufacture of ammonium perchlorate according to Kaye [81].

For high burning rate propellants a fine particle size ammonium perchlorate is required and can be produced by three processes according to Kaye [81]:

(a) In a jet mill in the atmosphere of nitrogen or helium at 82°C. The powder of AP of 5 μ is collected in trichloroethylene.

(b) By slurry grinding. A slurry of 85 parts of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) and 15% of AP and a small portion (0.15 parts) of a surfactant is ground for 160 hours to obtain a particle size of 1.72 μ.

(c) By freeze-drying. An emulsion made of AP in water and 1% Nopogen emulsifier and 0.1% Johnsons Wax. The emulsion is freeze-dried in a vacuum sublimator to give a product of particle size 0.37 μ. The Wax or some polymers such as 2-cyanoacrylate were added to prevent crystal regrowth.

Specification

The U.S. specifications [81] require 99.0–99.3% purity, total moisture 0.05–0.08%, surface moisture 0.02%, NH_4Cl 0.03–0.15%, $NaClO_3$ 0.02%, Bromates as $NaBrO_3$ 0.0–0.004%, K_2CrO_4 0.0–0.015%, iron (as Fe) 0.001% or (as Fe_2O_3) 0.0036%, ash (as sulphates) 0.25–0.30%, volatiles 0.04%.

Meyer [80] describes three grades of specification: A, B and C which are similar to the above, and in addition: water insolubles 0.01–0.03%, residue from sulphuric acid forming 0.3%, Na and K not more than 0.08%, $Ca_3(PO_4)_2$ 0–0.22%, pH 4.3–5.3 or 5.5–6.5.

Specifications also include particle size.
Meyer [80] mentioned seven classes:

(1) through 420–297 μ sieve, retained on 74μ sieve,
(2) and (3) through 297 and 149 μ sieve respectively,
(4) 50–70% through 210 μ sieve,
(5) through 297 μ sieve, retained on 105 μ sieve,
(6) 89–97% through 297 μ sieve,
(7) 45–65% through 420 μ sieve.

PERCHLORATES OF METALS (Vol. III, p. 230)

A considerable number of perchlorates of metals have been described in the monograph by Schumacher [46] and also in the Encyclopedia by Kaye [81]. A short review of the properties of metal perchlorates was given by Shidlovskii [85]. He compared the thermochemistry of their decomposition according to the general equation:

$$M(ClO_4)_n \longrightarrow MCl_n + 2n\,O_2 - \Delta H. \tag{10}$$

He pointed out that three decomposition groups exist:

(1) Perchlorates of K, Rb, Cs decompose with a very small thermochemical effect, for example with $KClO_4$ it $-\Delta H = 0.6$ kcal/mol.

(2) Perchlorates of Li, Na, Mg, Ca, Ba which decompose with a small exothermic effect: Li and Na of $-\Delta H = ca.$ 6 kcal/mol. and Mg and Ba of the same value for equivalent. Thus for $Ba(ClO_4)_2$ $-\Delta H = 12.8$ kcal/mol.

(3) Perchlorates with a marked exothermic decomposition, for example silver perchlorate which gives $-\Delta H = 22.3$ kcal/mol. Silver perchlorate possesses explosive properties (Vol. III, p. 232).

It was found that when free of any organic substance, it is insensitive to mechanical action. However with a small amount of ethyl ether it shows a high sensitivity to shock and friction and has caused a few accidents.

Recently a less explicable accident has occurred [109] with cobalt (II) perchlorate. The salt had been prepared by allowing aqueous perchloric acid to react with an excess of $CoCO_3$, filtering off the excess carbonate, reducing the volume and crystallizing out the salt. The explosion occurred when the caked mass of crystals was placed in a mortar and tapped gently to break it up. No organic matter is thought to have been present. Extreme caution should be taken in handling $Co(ClO_4)_2$ and similar salts.

The mechanism of decomposition of barium perchlorate was examined by Jacobs, Solymosi and Rasko [113].

OTHER PERCHLORATES (Vol. II, p. 483)

Hydrazine perchlorate (hyzazinium perchlorate)

$$NH_2\,NH_3^+\,ClO_4^-$$

Conant and Rooj [93] studied the crystal structure: they found it to be orthorhombic with m.p. 131–132°C and density 1.939. Carleton and Lewis [94] studied the phase system with water and reported m.p. 142.4°C and a hydrate $N_2H_4 \cdot HClO_4 \cdot \frac{1}{2}\,H_2O$ losing water at 61–64°C. M.p. 137–138°C of the perchlorate was also reported [95].

Heat of neutralization of $HClO_4$ with N_2H_4 was – 44.4 kcal/mol and heat of formation $-\Delta H_f = 42.9$ kcal/mol [96] and $-\Delta H_f = 40.7$ kcal/mol [97].

It can be prepared by neutralizing aqueous solution of hydrazine with $HClO_4$ [95] or by double exchange of hydrazine salt with an inorganic perchlorate dissolved in lower alcohols [98].

The deflagration of Hydrazine Perchlorate was studied by Levy, von Elbe and co-workers [111]. They found that it could be catalysed by copper chromite, potassium dichromate and magnesium oxide. The entropy of vapourization and dissociation:

$$N_2H_5ClO_4 \longrightarrow N_2H_4 + HClO_4 \qquad (11)$$

is 73 cal/deg. mole. (A similar figure was found for the entropy of dissociation of ammonium perchlorate into NH_2 and $HClO_4$: 71 cal thermal dissociation of deg. mole.) Grelecki and Cruice [112] examined also hydrazinium diperchlorate (see below) and found its decomposition to be autocatalytic. On the contrary monoperchlorate is not autocatalytic.

Volk and Schubert [61] examined the fragmentation in a mass spectrometer. They found NH_3^+, NH_4^+, H_2O^+, H_3O^+, $N_2H_4^+$, $N_2H_5^+$, ClO_2^+, $HClO_4^+$.

On heating it decomposes at 230°C [95], but Shidlovskii *et al.* [96] gives the ignition temperature 277–280°C. On detonation the volume of gases is 864 l/kg [96].

Lead block expansion is the order of 113% of Picric acid or 122% of TNT [81].

Hydrazine Diperchlorate

$$[NH_3NH_3]^{2+}(ClO_4)_2^-$$

m.p. 191°C.

The compound has the density 2.21.

Salts of Hydrazine Perchlorate and Chlorate Complexes
(Vol. III, p. 230)

Complex salts of hydrazine and perchlorate were described also by Maissen and Schwarzenbach [99] and in the Encyclopedia [81].

Nitrosyl Perchlorate (Vol. II, p. 484)

Fragmentation in a mass spectrometer was described by Volk and Schubert [61].

Hydroxylamine Perchlorate

$NH_2OH \cdot HClO_4$

m.p. 87.5–90°C

It forms hygroscopic crystals, decomposing at 120°C. Heat of formation was $-\Delta H_f = 66.2$ kcal/mol. It was prepared by reacting hydroxylamine sulphate with $BaClO_4$. Impact sensitivity was of 15 cm by 2 kg falling weight [81].

Methylamine Perchlorate (Vol. III, p. 484)

$CH_3\ NH_3\ ClO_4^-$

m.p. 255°C (d)

The crystal structure was reported by Stammler [100] and Zanazzi [101]. The substance passes through a phase transition at 178°C. Densities of phase II at 77°C is 1.58 c/cm³, phase I at 200°C is 1.58 g/cm³.

The temperature of explosion by heating was found to be 338°C [102]. Mass spectrometry was examined by a number of authors, most complete being the study by Volk and Schubert [61]. They found fragments at 260°C: CH_3^+, CHN^+, CH_2N^+, CH_3NH^+, $CH_3NH_2^+$, Cl^+, ClO^+, ClO_2^+, ClO_3^+, $HClO_4^+$ m/e.

Guanidine Perchlorate (Vol. III, p. 485)

Markwald and Struwe [103] described the method of making this substance from cyanoguanidine and ammonium perchlorate. Some physico-chemical properties were reported [104]. Heat of formation according to Krivtsov and co-workers [105] was found to be $-\Delta H_f = 74$ kcal/mol.

Guanidine perchlorate is a powerful explosive: its rate of detonation can reach 7150 m/s at $\rho = 1.67$, and lead block expansion 400 cm³ [106].

Nitroguanidine Perchlorate

This interesting substance, which is an exothermic compound, was obtained by Rosolovskii, Krivtsov and Titova [97]. Its enthalpy of formation is $-\Delta H_f = -51.5$ kcal/mol.

Fluoroammonium Perchlorate

$$NH_3F\,ClO_4^-$$

This substance was prepared by Grakauskas and Baum [107]: a solution of ethyl (or isopropyl)-*N*-fluorocarbamate in 70% $HClO_4$ was heated until CO_2 was evolved at 68°C. The excess of perchloric acid was removed under vacuum:

$$C_2H_5OCONHF + HClO_4 \longrightarrow NH_3FClO_4 + CO_2 + C_2H_5OClO_3. \qquad (12)$$

Fluoroammonium perchlorate has an appreciable vapour pressure, subliming at 46°C.

Nitronium Perchlorate (Vol. I, p. 19)

$$NO_2^+\,ClO_4^-$$

The substance forms hygroscopic crystals which melt on decomposition at 135°C without explosion.

The original product obtained by Hantzsch (Vol. I, p. 19) proved to be a mixture of nitronium perchlorate and perchloric acid monohydrate (Goddard and co-workers [116]). Nitronium perchlorate was obtained by distilling anhydrous perchloric acid onto an excess of dry dinitrogen pentoxide at −80°C and the mixture was kept *in vacuo* to remove volatiles. The product was composed of 89% nitronium perchlorate and 11% perchloric acid hydrate. Pure nitronium perchlorate was obtained by repeating the experiment in nitromethane with a large excess of N_2O_5 [117]. Cordes [114] examined the decomposition between 70 and 112°C and found gaseous products NO_2, Cl_2, ClO_2, NO_3Cl and O_2. M. D. Marshall and Lewis [115] established that at 65°C the major products were nitrosonium perchlorate and oxygen. Nitrosonium perchlorate further decomposes:

$$NO\,ClO_4 \longrightarrow NO_2 + Cl\,O_2 + \tfrac{1}{2}O_2$$

$$2\,Cl\,O_2 \longrightarrow Cl_2 + 2\,O_2.$$

PERCHLORIC ACID AND CHLORINE OXIDES

Thermal decomposition of ammonium perchlorate and perchlorates of other bases raised problems of the decomposition of perchloric acid and oxides of chlorine. This was extensively reviewed by Schumacher [46], Zinovyev [86], Jacobs and Whitehead [47], Pearson [87].

Perchloric Acid (Vol. III, p. 313)

Thermal decomposition of perchloric acid is a complicated process and the trend of decomposition depends on the temperature. The process is particularly complicated at temperatures below *ca.* 315°C. Above that temperature the reaction is homogeneous [8]. The following are products found in the region 200–440°C: Cl, Cl_2, O, O_2, H_2O and chlorine oxides [60, 88, 89].

Chlorine Oxides

Chlorine oxides are compounds of a relatively low stability, the most stable being Cl_2O and Cl_2O_7.

Chlorine monoxide (Cl_2O) is explosive if heated rapidly or overheated locally, but on careful heating the decomposition between 100° and 140°C is measurable [90].

Chlorine heptoxide (Cl_2O_7) was studied at temperatures of 100–120°C [91], it decomposed to chlorine and oxygen. The decomposition of liquid compound was examined [92] at 60–80°C.

The decomposition of other chlorine oxides are given in a review [47].

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CHAPTER 17

PRIMARY EXPLOSIVES: INITIATORS, INITIATING EXPLOSIVES, (IE)

(Vol. III, p. 129)

INTRODUCTION

With regard to the number of primary (i.e. initiating) explosives very little can be added to those already described in Vol. III. Thus the most used initiators are: Lead Azides, Lead Styphnate, Tetracene. Mercuric Fulminate which is the oldest and so far most popular initiator is gradually being withdrawn from use in some countries (e.g. in the U.S.A.) and replaced by lead azide. The other primary explosives, such as cyanuric triazide and diazodinitrophenol are good initiators but have not yet received wider application. A few more primary explosives have proved to be efficient initiating agents such as: silver, cadmium and cupric azides, triazidotrinitrobenzene, salts of acetylene, double salts of styphnic acid (lead salt) and tetracene, hexamethylenetriperoxide diamine.

A large group of explosives exists which have initiating properties: they are complex salts of metals with bases such as ammonia, amines, hydrazine etc. (Vol. III, p. 230). There is insufficient information on the properties of these compounds, their stability and their action on metals, therefore they cannot be recommended as yet for practical use.

A good initiating explosive (IE) should correspond to numerous requirement, such as:

1. Good initiating properties, that is, a small charge of IE should bring an explosive to detonation. This is usually connected with a short time of burning to detonation. A classic example is lead azide which has a remarkably short time of burning to detonation according to Patry and Laffitte [46, 47].
2. Safe handling and use in manufacture of elements of ammunition, such as pressing into the elements.
3. Ease of filling the initiating elements and ease of safe pressing.
4. Safe use of such elements, for example avoiding premature detonation when striking an object.

5. Stability on storage at room temperature and elevated temperatures (e.g. up to 150°C) and in some types of charges at low temperature. They should not react with carbon dioxide in atmosphere.

6. Absence of corrosive effect of the substance on metal used for initiating elements (cups and tubes).

7. Ease of safe manufacture of the substances.

Failure to answer one of the above conditions may cancel the practical application of the substance.

An important property of IE is their ability to burn to detonation under reduced pressure. This is of significance to space research, and will be discussed below.

BURNING OF IE UNDER REDUCED PRESSURE

There has been some controversy as to whether initiating explosives can burn and eventually detonate under reduced pressure. The earlier literature reported that they do not burn in a 'high vacuum' [39]. Muraour and Schumacher [40a] found that initiating explosives can burn to detonation under pressure of 10^{-3} to 10^{-4} torr. This was not in agreement with the earlier finding of Burlot [41a]. Burlot [41b] reported that different initiating explosives are characterized by a critical low pressure: the explosive cannot burn and detonate if the pressure falls below that limit. The critical pressure amounts to as much as 15 torr for mercuric fulminate and 2×10^{-2} torr for lead azide. Belaev [42, 44], Belaev and Belaeva [43] seem to confirm the view of Burlot, although they did not examine the pressure below 2–3 torr.

T. Urbański and Stanuch [45] undertook experiments to clarify the existing discrepancy particularly in view of the importance of the problem.

Their conclusion was that initiating explosives can be divided into five classes according to their behaviour when ignited with a resistance wire under reduced pressure. Here is their classification.

(I) IE which readily detonate when ignited either as loose powder or pressed pellets at pressure as low as 10^{-5} torr. Lead, silver and mercuric azides, silver and cadmium fulminates, lead styphnate and *m*-dinitrobenzdiazonium perchlorate belong to this group of compounds. All the above substances are characterized by a very short period of burning preceding detonation.

(II) IE which readily detonate when ignited as pellets at pressure as low as 10^{-4} torr. When in the form of loose powder they detonate under a pressure above 1 torr. Cyanuric triazide and hexamethylenetriperoxide diamine belong to this group of compounds.

(III) IE which burn without detonation when ignited as pellets under pressure of the order of 10^{-4} torr. Under atmospheric pressure they burn to detonation. When in the form of a loose powder they partially burn under pressure of 1 torr but under atmospheric pressure can burn to an explosion. Mercuric fulminate belongs to this group of compounds.

(IV) IE in the form of pellets which can detonate when ignited under atmospheric pressure, but do not detonate when the pressure is of the order 100–400 torr. At lower pressures of the order of 10^{-4} torr they do not burn. In the form of loose powder they burn under atmospheric pressure but do not detonate. Dinitrodiazaphenol and tetrazene belong to this group of compounds.

(V) Substances of this group do not burn to detonation even at atmospheric pressure when the pellets are not confined. A strong confinement is needed to bring their burning to detonation. Trinitrotriazidobenzene belongs to this group of compounds.

One more remark should be added to the behaviour of initiators as under (I) and (II) – still higher vacuum should be examined. Perhaps under pressure lower than 10^{-5} torr the primary explosives of groups (I) and (II) may behave differently from above and decompose without explosion. Thus the classification as above is valid only in limits for vacuum application.

Recently a monograph on initiating explosives written by Bagal [1] appeared. It contains chapters on:

1. Fulminates
2. Azides
3. Styphnates
4. Diazo compounds
5. Tetrazen and Tetrazoles
6. Peroxides
7. Acetylenides

Two other monographs have appeared which have been dedicated to azides: a collective volume edited by Patai [2] and two collective volumes on metal azides edited by Fair and Walker [3]. Also reviews have appeared on alkyl and aryl azides by Boyer and Canter (Vol. III, p. 196), and organic azides by L'abbé [4].

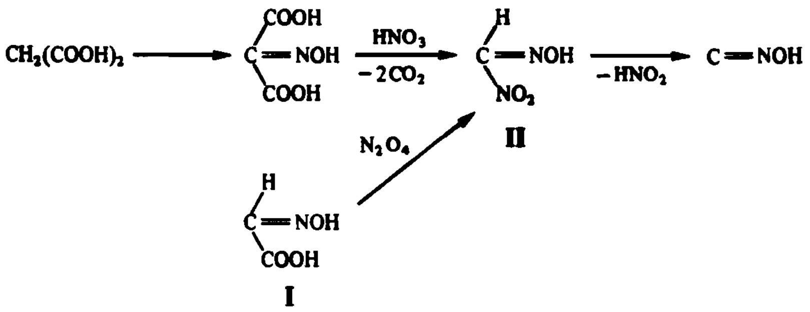
MERCURIC FULMINATE (Vol. III, pp. 129, 139)

The monograph by Bagal [1] contains a detailed description of the early history of the discovery of reactions leading to the formation of mercuric fulminate which began in 1800 thanks to the work of Howard (Vol. III, p. 129). Further work was done by Liebig [5], Liebig and Gay-Lussac [6], Gérard [7] and a number of other authors [8–18]. The correct structure of fulminic acid was given by Nef [19], supported by L. Wöhler and Teodorowits [20] and later by Wieland and Hess [21].

Polymerization of fulminic acid was studied by Wieland and Hess [21] and much later by Birkenbach and Sennewald [22]. These works led to rationalize the polymerization to a trimer given in Vol. III, p. 133 as formula VII.

Dansi [23] criticized the scheme of Wieland (Vol. III, p. 135). He could not obtain fulminates of mercury and silver by acting with their nitrates on isonitrosoacetic acid. The salts of isonitrosoacetic acid did not yield fulminates when acting with nitric acid (equations 5–8, Vol. III, p. 135). This casts some doubt on the accuracy of Wieland's scheme.

The structure of mercuric fulminate was also confirmed by Angelico through the ingenious formation of the compound from malonic acid (Vol. III, p. 136). Ponzio [24] found that nitrogen dioxide reacted with oxaminoacetic acid (I) yielding methylnitrolic acid (II) and therefore the reaction of Angelico-Ponzio should be presented by scheme (1) according to [1]:



(1)

Physical Properties

The problem of difference in colour of mercuric fulminate (grey and white crystals) does not seem to be fully solved. The view of Solonina (Vol. III, p. 138), Philip [25], Langhans [26], Marshall (Vol. III, p. 138) that the grey colour mercuric fulminate is due to some organic impurities seems to be correct. Crystallization of the substance from a solvent always yielded a white substance. The coloured products are probably resinous polymers of fulminic acid. The latter contains a double bond and is liable to polymerize. Whitening of mercuric fulminate by adding cupric salts appears to be an optical effect.

The density of mercuric fulminate on pressing into a No. 8 copper detonator case is according to Wöhler and Roth [27]:

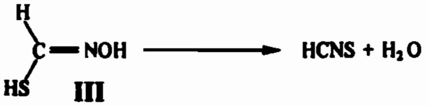
Pressure kg/cm^2	100	250	500	1000	2000
Density g/cm^3	2.36	2.61	2.99	3.47	3.76

Technical mercuric fulminate contains (according to Bagal [1]) mercuric oxalate, mercurous oxides, inclusion of the reaction liquor, mercuric chloride. Bagal also mentioned the presence of metallic mercury which proved to be not always correct according to Solonina [28]. He examined samples of grey mercuric fulminate by keeping them and frictioning on gold plates and no formation of amalgamate was noticed.

Many authors stated that keeping most of the solutions of mercuric fulminate for a longer time leads to the decomposition of the substance. According to Solonina [28] a solution of mercuric fulminate in 22% aqueous ammonia produced a decomposition of the dissolved substance and mercuric oxide precipitated after 12 hours of keeping the solution at room temperature. Pyridine – a good solvent of mercuric fulminate – may also bring about decomposition with a precipitation of metallic mercury [26, 28]. Also a yellow coloured precipitate may be formed with a low content of Hg (*ca.* 58.5%) [1].

Chemical Properties

As pointed out in Vol. III (p. 140) mercuric fulminate is subjected to decomposition under the action of concentrated acids. Aqua regia produces chloropicrine. Thiocyanic acid gives an exothermic reaction with the formation of mercuric sulphide. If the temperature rises high – metallic mercury may be precipitated [1]. Nef [19] examined the action of hydrogen sulphide on silver fulminate and came to the conclusion that the salt of thioformhydroxamic acid (III) is formed. Cambi [29] tried to isolate the free acid. However it decomposed readily yielding thiohydrocyanide:



III

(2)

The reactions of metals with mercuric fulminate was described for the first time by Cheltsov in 1883 [30]. Dry mercuric fulminate did not react with metals – such as copper or brass, but in the presence of moisture a gradual formation of amalgamates occurs with time. Subsequently all elements containing mercuric fulminate and pressed into metal casing should be protected from moisture by varnish or air-tight casing.

Hygroscopicity of mercuric fulminate was examined by Kast [31]. He found that technical mercuric fulminate is non-hygroscopic: in 100% moisture atmosphere during 80 days at room temperature its weight increased by 0.16%. Mercuric fulminate reacted with potassium chlorate in a moist atmosphere and mercuric oxide resulted.

Sensitivity to impact. As a typical IE, mercuric fulminate is very sensitive to impact. Bubnov (according to [1]) reported that grey mercuric fulminate is slightly more sensitive to impact than the white species.

Chemical Stability and Behaviour at High Temperature (Vol. III, p. 141)

The earliest experiments on the stability of mercuric fulminate belong to Hoitsema [32] and Solonina [28]. Hoitsema examined the behaviour of mercuric fulminate under reduced pressure.

Solonina determined the ignition temperature and found it varied within the limits 157–172°C. When heating started at 100°C, the temperature was invariably 160°C.

Kast and Haid [33] found the following data: mercuric fulminate heated at the rate of 20°C/min exploded at 170–175°C, when kept at constant temperature explosion occurred:

at 190°C after 8–10 sec.
200°C after 7–8 sec.
205°C after 5 sec.

Behaviour at Low Temperature

Kling and Florentin [34] examined the behaviour of mercuric fulminate at low temperature: from −80° to −183°C and found that the velocity of detonation does not change with temperature at the density of 1.25 the figures were: 2365 m/s and 2350 m/s at room temperature and at −183°C respectively.

Clark [35] investigated the initiating properties of mercuric fulminate at different temperatures: +25°, −80° and −183°C to test the applicability of detonators in charges with liquid oxygen. He found a lowering of initiating power of detonators with a lowering of temperature, but the velocity of detonation did not change – in agreement with the observation of Kling and Florentin.

Action of Light

The following information on the work of Farmer [36] should be added to those given previously (Vol. III, p. 146). He examined the influence of sun-light on both grey and white samples and found white samples to be more sensitive to the action of light. Thus after 320 hours of irradiation white and grey samples evolved 0.37 and 0.14 ml of gas respectively. Patry and Laffitte [37] examined the influence on the induction period of irradiation of mercuric fulminate with ultraviolet light. The induction period was very much shortened by irradiation, for example, at 160°C freshly made sample and irradiated sample gave the induction periods of 252 and 9 sec. respectively.

According to Borocco [38] mercuric fulminate irradiated with ultraviolet light *in vacuo* was partly decomposed with the evolution of nitrogen and carbon monoxide according to the equation

$$Hg(ONC)_2 \longrightarrow Hg + 2\,CO + N_2. \qquad (3)$$

He also compared burning of samples: irradiated and previously heated to 100°C and found a similarity between the action of irradiation and pre-heating.

Burning under Reduced Pressure

As previously pointed out (p. 464) mercuric fulminate belongs to the group of IE which can burn to detonation under atmospheric pressure or pressure near to atmospheric. Under pressure of 10^{-4} torr it burned without detonation. Muraour and Wohlgemuth [48] examined the influence of the temperature of the charge of mercuric fulminate on burning under reduced pressure. At room temperature a pellet pressed under 3000 kg/cm² kept in vacuo, burned quietly. If preheated to 130°C it detonated within 10 min of keeping at this temperature without using an ignition wire.

'Dead pressing' of mercuric fulminate was described in Vol. III, p. 146. Muraour and Wohlgemuth [48] explain this phenomenon in terms of 'preheated' samples of the IE. If the sample is not 'dead pressed' it is sufficiently porous for the hot gases of decomposition to penetrate inside the charge and produce 'preheating' of the substance.

Initiating Properties of Mercuric Fulminate

Gedymin [49] used an original method for determining initiating properties of a mixture of 95% mercuric fulminate with 5% $KClO_3$. He determined the ratio (p) of the smallest ('critical') mass (m) of the initiating charge to the surface area (s) of the charge of the initiated explosive pressed into a cylindrical metal tube:

$$p = \frac{m}{s}.$$

For tetryl and TNT p is 1.12 and 1.52 respectively. The figures express the easier initiation of tetryl than of TNT.

Extensive experiments by Koester [50] on the initiating properties of mercuric fulminate are given in Table 72.

TABLE 72. Critical charges of mercuric fulminate

Initiated explosive	Critical charge g
PETN	0.35
Tetryl	0.36
TNT	0.38
Tetryl + 10% paraffin wax	0.36
Tetryl + 20% paraffin wax	0.44

Koester also examined the influence of the metal casing on the initiation properties of mercuric fulminate. The critical charge was found to be smaller in a hard metal (e.g. steel) than in a soft one (e.g. copper). The figures were: 0.24 g (steel) and 0.38 (copper).

Other Salts of Fulminic Acid (Vol. III, p. 157)

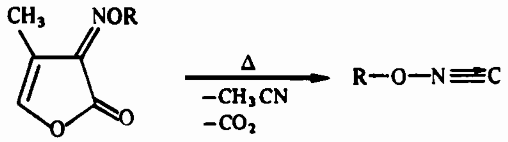
The only other salt of fulminic acid which was in some limited use was silver fulminate. However it no longer seems to be in use, and other salts were also of no use.

Manufacture of Mercuric Fulminate

No changes in the manufacture as described in Vol. III, p. 149 can be found. The only note of historical interest is that experiments were made by replacing ethanol with methanol in the manufacture of mercuric fulminate. Negative results were reported by Dumas and Peligot [51]. However Stahlschmidt claimed to have obtained mercuric fulminate from methanol as early as 1860 according to [1]. The discrepancy was explained later, e.g. [20], that methanol of Stahlschmidt contained dimethyl acetal – a derivative of acetaldehyde, and this discovery led to the finding [20] that mercuric fulminate can be obtained with a high yield and purity from acetaldehyde.

Esters of Fulminic Acid

Recently Wentrup, Winter and co-workers [182] described the reaction leading to the formation of esters of fulminic acid by vacuum flash pyrolysis (300–600°C) and matrix photolysis of 4-oximinoisoxazol-5(4H)-ones



The esters are unstable and decomposed above −100°C: when R = CH_3, it yielded formaldehyde and hydrocyanide.

HYDRAZOIC ACID, ITS DERIVATIVES AND SALTS (Vol. III, p. 161)

The chemistry of hydrazoic acid derivatives have recently created a wide literature [2, 3, 126, 184] owing to the fact that azides are convenient starting substances in preparative chemistry. This was reviewed by L'abbé [4] and partly by Boyer [52] in his recent paper on covalent oxygen bonding of nitrogen attached to carbon. Also a review on carbamoyl azides appeared [53].

Decomposition of Azides

Decomposition of azides very often begins with formation of nitrenes which contain uncharged nitrogen radical intermediate according to reaction (4)

$$R{-}N_3 \xrightarrow{\Delta \text{ or } h\nu} R{-}\dot{N}\cdot + N_2. \tag{4}$$

Chemistry of nitrenes was also reviewed [54, 55].

The formation of free radical $H\dot{N}\cdot$ by decomposition of hydrazoic acid has been suggested by a number of authors since 1928 (see Vol. III, p. 167). This was substantiated by experiments on the decomposition of HN_3 by the flash photolysis of Thrush (Vol. III, p. 167). The formation of nitrene radicals from azides by flash photolysis was reported simultaneously and independently by Koto [56], Reiser *et al.* [57–59]. Reiser rationalized the reaction derived from flash photolysis of formation of azo compounds (5):

$$R\dot{N}\cdot + RN_3 \longrightarrow RN = NR + N_2. \tag{5}$$

Nitrenes have triplet ground states. At room or higher temperature they can behave as triplet diradical and singlet electrophilic species. They have a very short time of several microseconds, but can undergo stabilization by a number of reactions, such as: isomerization to amines, dimerization to azo compounds, ring closure to heterocyclics, various addition reactions [4]. Curtius rearrangement [60] is one of the classical examples of passing through the nitrone formation.

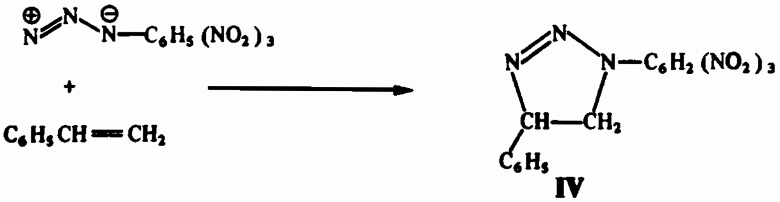
Infra-red study of thermal decomposition of N_3^- ion (e.g. KN_3 at 345–350°C) shows the formation of NCO^- as a by-product of CO_2 trapped during pressing and the possible reaction:

$$N_3^- + CO_2 \longrightarrow NCO^- + \tfrac{1}{2}\,O_2 + N_2. \tag{6}$$

Azido compounds can be convenient intermediates in the synthesis of natural products containing amino group. Thus crystalline 4-amino hexoses can be formed by hydrogenation of 4-azido hexoses [70].

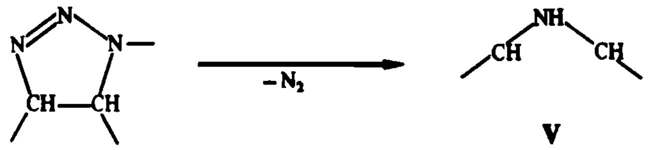
Heterocyclics from Azides

An important reaction is 1,3-dipolar cycloaddition reviewed by Huisgen [61]. An example can be seen from the reaction of styrene (dipolarophile) and picryl azide (1,3-dipole) yielding a triazoline (IV):



IV

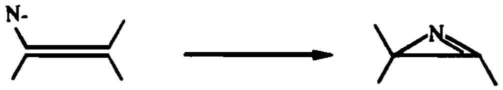
1,3-Dipolar addition should also occur between nitrenes and acetylenes [61]. The triazoles (IV) can lose N_2 yielding aziridines [72] (V)



IV

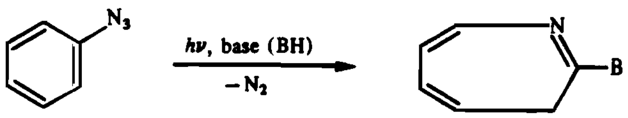
V

Pyrolysis of vinyl azides offers an interesting method of forming azirines [62] (VI)



VI

A similar result was obtained by photolysis of vinyl azides. The reaction can lead to azepines (VII) [63] possibly through the intermediate formation of aziridines [64] (as known, diazepines are an important group of tranquillizers [65]).

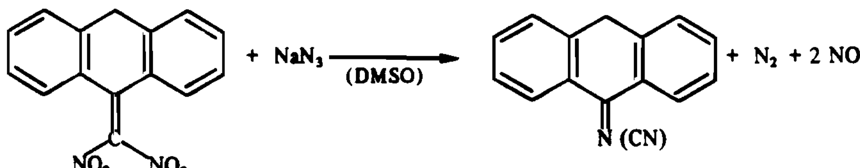


VII

The reduction of vinyl azides with sodium sulphite followed by hydrolysis can lead to ketones [71].

Other Reactions of Azide Anion and Radical

An unusual reaction was recently reported by Hoz and Speizman [65] on the reaction of azides with nitroalkenes, resulting in the formation of *N*-cyano compounds (VIII)



VIII

The mechanism of the reaction is not quite clear.

Another interesting reaction comes from the fact observed by Forster and Fierz [67] that the azido-group can function under basic conditions as an *intra-*

molecular oxidizing agent. Thus α-azido ketones are transformed into α-diketones. The reaction was mentioned in the review by Boyer and Canter [68] and recently studied [69] as a two step reaction (7):

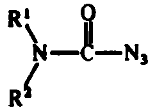
$$C_6H_5CH_2CN \xrightarrow[\text{2. excess } N_3^-/(CH_3)_2SO]{\text{1. NBS/CCl}_4} \underset{90\%}{C_6H_5CN} + N_2 + CN^- \qquad (7)$$

Minisci [186] described the addition of azide radical to double bonds. Particularly interesting is the addition of $N_3^{\bullet}$ in allilic position.

Some Organic Azides

Among different groups of organic azides a few are of some interest because of their properties.

Such are carbamoyl azides [53] of a general formula (IX)



IX

There are three methods of preparing IX:

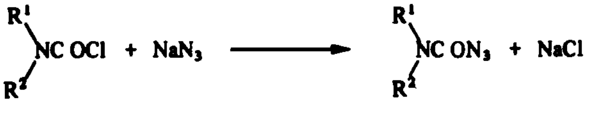
1. Diazotization of semicarbazide or other compounds containing the carbohydrazide grouping:

$$RNHCONHNH_2 \xrightarrow{HONO} RNHCON_3 + H_2O \qquad (8)$$

2. Reaction of isocyanate with hydrazoic acid:

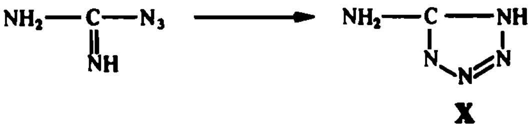
$$RNCO + HN_3 \longrightarrow RNHCON_3 \qquad (9)$$

3. Reaction of carbamoyl chlorides with metal azides:



$$R^1R^2NCOCl + NaN_3 \longrightarrow R^1R^2NCON_3 + NaCl \qquad (10)$$

An imino-derivative of carbamoyl azides, guanyl azide can react forming 5-aminotetrazol (X) [73], a substance with explosive properties:



X

No similar cyclization can occur with carbamoyl azide.

An interesting azide which is in use as a source of triazolines and aziridines [72] is a cyanogen azide, $CN{\cdot}N_3$. It can be obtained according to Marsh and Hermes [74] as a colourless explosive oil by a simple reaction of sodium azide with cyanogen chloride. It is not stable at room temperature but in a 27% solution in acetonitrile at 0° to −20°C can be kept undecomposed (see also [75]). Later on Coppolino reported [76] that cyanogen azide can be decomposed when kept in solution even at −20°C. With alkenes it does not give very stable traizolines.

Carbon azide $C(N_3)_4$ is not known. However Müller and Dehnicke [105] succeeded in obtaining a complex salt with triazidocarbonium ion (XI) by refluxing antimony azidochloride in carbon tetrachloride:

$$Sb(N_3)Cl_4 \xrightarrow[\text{reflux (4 hr)}]{CCl_4} [C(N_3)]^+ (Sb\,Cl_4)^-$$

XI

It decomposed after melting at 145°C.

Danger of Handling Azides

The danger of handling apparently stable organic azides has recently been described [77]. Thus:

1. Ethyl azide exploded when kept at −55°C for a few minutes, the reason for the explosion could not be elucidated.

2. *p*-Toluenesulphoazide exploded during distillation under reduced pressure.

3. A derivative of siladiazide $(CH_3)_2Si(N_3)_2$ exploded after being kept for three years when the flask with the substance was opened. Also $Cl_2Si(N_3)_2$, $ClSi(N_3)_3$, $Si(N_3)_4$ – residues from the distillation of the products of the reaction between $SiCl_4$ and NaN_3 in tetrahydrofurane – exploded. This was probably caused by HN_3 evolved from the above products. This is not surprising in the light of the observation below.

Hydrazoic acid (Vol. III, p. 166) is relatively stable, but can explode spontaneously on handling. Curtius and Radenhausen [78] described two unexpected explosions: (1) when the substance was introduced into a barometer vacuum tube, (2) when the glass vessel containing the acid was removed from a cooling bath. A suspicion was advanced that hydrazoic acid stored for a long time in a glass container is more dangerous than the same acid freshly prepared, probably due to impurities taken from the glass [79–81].

4. Borazides: $(CH_3)_2BN_3$, $(Cl_2BN_3)_3$, $B(N_3)_3.Py$ exploded without any apparent reason when poured or taken with a nickel spatula.

5. Esters of azidoacetic acid, for example N_3CH_2COOt-Bu can explode above 80°C [82].

6. Acyl azides can present danger in handling, for example during distillation *in vacuo*. An accident with toluene-sulphonyl (tosyl) azide has been described.

Cyanic Triazide (Vol. III, p. 194)

No practical application has been found for this interesting compound owing to its sensitivity to handling, impact, volability and hygroscopicity [142–144]. Nevertheless its structure aroused a certain amount of interest and the X-ray structure was examined [145]. It confirmed the structure given in Vol. III, p. 194, formula XI.

Explosive Properties of Hydrazoic Acid

Médard [88] reported thermochemical data for hydrazoic acid:

$$\text{heat of formation } -\Delta H_f = 71.66 \text{ kcal/mol (gas)}$$
$$= 64.37 \text{ kcal/mol.}$$

According to Bagal [1] aqueous solutions of hydrazoic acid can detonate: 70% aqueous HN_3 showed the rate of detonation 7300 m/s. Anhydrous hydrazoic (liquid) gave 8100 m/s.

As previously mentioned hydrazoic acid stored for a long time is more dangerous in handling than the product freshly prepared.

Gentle friction can produce an explosion of hydrazoic acid. An accident has been described of an explosion of the substance, caused by the friction of a piece of glass in a flask put there to produce more uniform boiling [94].

Ammonium Azide (Vol. III, p. 190)

This interesting salt attracted attention as it produces a considerable amount of gas: 1148 l/kg the highest figure for all explosives.

It is a crystalline substance, readily soluble in water and 80% ethanol, insoluble in ether and benzene. It melts at 160°C and begins to decompose. It is volatile and sublimes below 250°C under 150 mmHg. The vapour pressure at different temperatures was determined [1]:

at	48.0°C	85°C	125°C	134.2°C
was found	4.5	55.1	508.1	782.1 mm.

When heated under atmospheric pressure it decomposed while dissociating into NH_3 and HN_3 and finally the HN_3 exploded [103].

The easiest method of preparing ammonium azide [125] consists in the reaction of sodium azide with ammonium chloride in dimethylformamide at 100°C. After the reaction subsided, all was cooled to 60–70°C and dimethylformamide was distilled under reduced pressure. Ammonium azide crystallized out.

As previously mentioned (Vol. III) a practical application has not been found for the substance due to its volatility.

PHYSICO-CHEMICAL AND EXPLOSIVE PROPERTIES OF METAL AZIDES

The fundamental problem of why some azides (e.g. KN_3) are not explosive whereas others (e.g. $Pb(N_3)_2$) are, is still not fully understood. Nevertheless a great amount of information has been collected to date on various physico-chemical properties of azides which can partly throw some light on the problem (see Table 73, Fig. 79 and [189]).

They are assembled in Vol. 1 of [3] and include the chapters:

Introduction, R. F. Walker (p. 1),
(1) Synthesis and the Chemical Properties, T. A. Richter (p. 15),
(2) The Growth of Crystals, W. L. Garrett (p. 87),
(3) The Crystal Structures, C. S. Choi (p. 97),
(4) Molecular Vibrations and Lattice Dynamics, Z. Iqbal, H. J. Prask and S. F. Trevino (p. 131),
(5) Electronic Structure of the Azide Ion and Metal Azides, T. Gora, D. S. Downs, P. J. Kemmey and J. Sharme (p. 193),
(6) Slow Thermal Decomposition, P. G. Fox and R. W. Hutchinson (p. 251),
(7) Imperfections and Radiation Induced Decomposition, W. L. Garrett, P. L. Marinkas, F. J. Owens and D. A. Wiegand (p. 285),
(8) Fast Decomposition in the Inorganic Azides, M. M. Chaudhri and J. E. Field (p. 383),
(9) Stability and the Initiation and Propagation of Reactions in the Azides, J. Alster, D. S. Downs, T. Goza, Z. Iqbal, P. G. Fox and P. Mark (p. 449).

Vol. 2 of [3] contains a description of more practical problems:

Introduction, R. F. Walker (p. 1)
(1) Processes for the Manufacture of Lead and Silver Azide, T. Costain and F. B. Wells (p. 11),
(2) Analysis of Azides for Assay, and in Complex Media, H. Kramer (p. 55),
(3) Handling, Storability, and Destruction of Azides, B. D. Pollock, W. J. Fisco, H. Kramer and A. C. Forsyth (p. 73),
(4) The Sensitivity to Impact and Friction, L. Avrami and R. Hutchinson (p. 111),
(5) Electrostatic Sensitivity, M. S. Kirshenbaum (p. 163),
(6) Sensitivity to Heat and Nuclear Radiation, L. Avrami and J. Haberman (p. 199),
(7) The Role of Azides in Explosive Trains, M. Voreck, N. Slagg and L. Avrami (p. 249).

The reader, interested in the manufacture and use of azides should consult both volumes. Many problems described in the volumes are outside the scope of the present book.

Optical Properties

The optical and electronic properties of azides have been reviewed [3, (Vol. I, p. 224)]. So far it has been suggested that there are similarities between the alkali azides and halides but recently attention has been paid to the identification of defect centres formed by irradiation of azides. Deb [106] carried out experiments with thin films or single crystals of Na, K, Rb and Cs azides between 140 and 280 nm at low temperatures, such as 4–77 K. He noticed an induced luminescence in all alkali azides. Earlier work by Audubert [107] showed a faint emission of ultraviolet light from various azides during thermal decomposition. Singer and Mueller [108] observed chemiluminescence and electron emission from thermally decomposing alkali azides.

Photoconductivity of azides, including $Pb(N_3)_2$ was examined by a number of authors [109–111].

Slow Decomposition of Azides

Slow thermal decomposition was examined by Garner (Vol. III, p. 171). It was shown [112] that when silver azide is heated, silver is formed in an oriented way through the azide lattice. The rapid growth of nuclei by the surface migration of metal in lead azide seems to be demonstrated [113]. Choi and Boutin [114] showed the existence of azide radicals in the course of the decomposition.

Some substances, including impurities, enhance the decomposition of azides. The impurities can be present in the course of preparation of azides or formed during their storage. It is known that the presence of carbon dioxide in air may produce a decomposition of lead azide. Also water vapour in air even at room temperature may accelerate the decomposition. This problem was tackled by Reitzner [115]. He found that the induction period was the result of the reaction of water vapour with lead.

The problem of the action of radiation on azides, particularly lead and barium azide has been reviewed [116]. Irradiation prior to thermal decomposition often effects a reduction or elimination of the induction period, a decrease in activation energy and an increase in the rate of decomposition. Zakharov and co-workers [117] have found that the application of a moderate electric field can affect the rate of thermal decomposition of azides.

Through irradiation the optical density of azides increases as shown by Roth [118] and Wiegand [119]. The experimental facts supported the hypothesis that colloidal metal was produced by irradiation of lead azide and tallium azide. Colloidal disorder can be created by radiation. Lead produced by photodecomposition is reactive and can form some products on exposure to air. Thus basic lead carbonate was found lead azide irradiated with X-rays [120, 121]. Lead azide expands along one crystallographic direction under the action of X-rays [122] and nitrogen in the form of N_2 can be trapped by the irradiated lattice

[123]. The visual colouration of lead azide was strongly suppressed by hydrostatic pressure of the order of 10 kbar [124].

Among different regularities a remarkable relationship exists between the heat of formation (ΔH_f) of a number of azides and infra-red frequency ν_2 ranging between 620 and 650 cm^{-1}. This is shown in Fig. 78 (Explosive azides) form a group separated from non-explosive ones. N_3^- ion becomes more asymmetric in the more covalent salts making those lattices thermodynamically less stable [102].

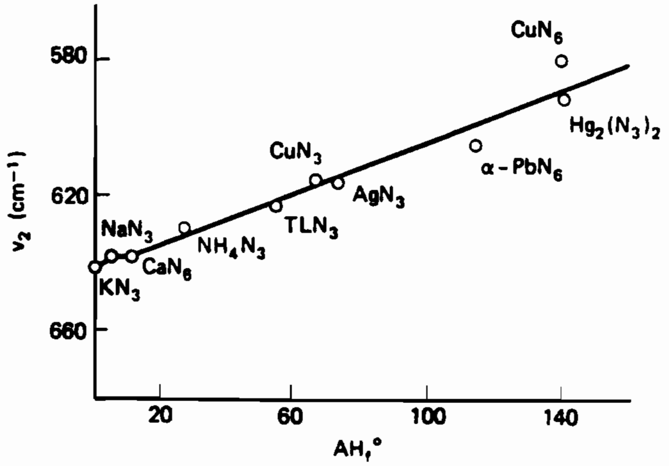


FIG. 78. Enthalpy of formation of azides ΔH_f° against infra-red frequency 580–600 cm^{-1}, according to [102].

Gray and Waddington [103, 104] determined experimentally and calculated enthalpies for the formation of azides. A great difference exists between non-explosive and explosive azides, as can be seen in Table 73.

TABLE 73. Azide enthalpies of formation ($-\Delta H_f$)

NaN_3	5.1 kcal/mol
KN_3	−0.3
$Ca(N_3)_2$	−2.4
$Ba(N_3)_2$	−5.3
α-$Pb(N_3)_2$	115.5
Ag N_3	74.2
$Cu(N_3)_2$	140.5

The above figures and Fig. 78 throw some light on the problem (p. 475) of why lead and silver azides possess marked initiating properties when the others do not.

Fast Decomposition and Explosion

A considerable amount of work has been carried out on the fast decomposition of azides. This was initiated by heat, friction, impact, shock, light, electric field and atomic particles.

Thermal initiation is given in Table 74.

TABLE 74. Thermal initiation of azides

Azides		Temperature of initiation, and melting, °C
Potassium azide	KN_3	350
Silver azide	AgN_3	251, explodes above the m.p.
Tallous azide	$Tl\,N_3$	334
Cuprous azide	$Cu\,N_3$ or $Cu_2(N_3)_2$	melts at *ca.* 205
Mercurous azide	$Hg\,N_3$	melts at *ca.* 210 and then explodes
Mercuric azide	$Hg(N_3)_2$	melts at *ca.* 195 and explodes at *ca.* 460
Cadmium azide	$Cd(N_3)_2$	explodes
Lead azide	$Pb(N_3)_2$	explodes

Impact sensitivity of lead and silver azides depends on the size of crystals or pellet thickness. The larger the crystals, the more sensitive they are. This and other problems related to the initiation of primary explosives are discussed by Bowden and Yoffe [125] and extensively reviewed by Chaudhri and Field [3 (Vol. 1, p. 383)].

LEAD AZIDE (Vol. III, p. 169)

Usually the advent of lead azide as a primary explosive is connected with the first patent by Hyronimus [83] in 1907. However, according to the literature [84] the first experiments with lead azide were carried out in Spandau (Germany) as early as 1893. They ended with a tragic accident and all experiments with lead azide were suspended. A number of doubts were expressed on the practical use of lead azide as an initiator [85, 86]. Also Kast [87] in his well known book raised the problem of whether lead azide and azides of other heavy metals could be used as primary explosives.

This view has prevailed in many countries. In the U.S.S.R. lead azide entered industrial production in 1929 (Bagal [1]). Between 1920 and 1930 a considerable amount of work was dedicated to the production of lead azide which would be less hazardous to manufacture and thus dextrinated product was manufactured.

Properties of Lead Azide

It was originally thought that lead azide existed in two allotropic forms: α and β (Vol. III, p. 169). Now it is accepted that the substance is polymorphic and exists in four forms: α, β, γ and δ. The α-orthorhombic is the only one acceptable for technical application. It is the main product of precipitation with traces of the other forms present [89]. The monoclinic β-form is stable when dry, but recrystallizes as the α-form. The presence of some organic dyes (e.g. eosin) enhances the formation of β-form and hydrophile colloids inhibit its formation. Breaking a needle of β-form may produce an explosion (contrary to the views of some authors; Vol. III, p. 173). The monoclinic γ-form is less stable than α and β [90]. It can be obtained from pure reagents at pH 3.5–7.0 or in the presence of vinyl alcohol. The triclinic δ-form precipitates from pure reagents at pH values of between 3.5 and 5.5 [90]. Both forms γ and δ are usually precipitated simultaneously and can be separated (with care!) by hand.

Apin (according to [1]) described a method of preparing needle like β-modification through a slow diffusion of aqueous solutions of sodium azide and lead nitrate.

Among different modifications of lead azide, basic salt $N_3Pb(OH)$ was prepared by Wöhler and Krupko [91] and showed less pronounced explosive properties: it deflagrated without detonating. Several basic lead azides have been prepared by Feitknecht and Sahli (Vol. III, p. 178).

An attempt was made to obtain $Pb(N_3)_4$ [92] from PbO_2 and hydrazoic acid. The product $Pb(N_3)_4$ was unstable and readily lost nitrogen to form $Pb(N_3)_2$.

Crystal Structure of α-$Pb(N_3)_2$

The crystal structure of α-$Pb(N_3)_2$ was examined with the help of three dimensional neutron-diffraction by Choi and Boutin [93]. These authors found four crystallographically distinct azide groups in a unit cell: azide (I), (II), (III) and (IV) – Fig. 79. Azide (I) is coordinated to four Pb atoms, two at each end. It is symmetric in both coordination and in N–N distances. Azide (II) is also surrounded by four Pb atoms but the coordination is asymmetric. The structure of azide (III) is very similar to azide (II) but the structure (III) is more symmetrical than (II). Azide (IV) is strongly asymmetric in both coordination and N–N distances.

Each Pb atom is surrounded by eight azide groups with bond lengths between 2.57 and 2.90 Å. It is further surrounded by four Pb atoms at distances 4.2–4.5 Å.

Spontaneous Explosions of Azides (Vol. III, p. 173)

Spontaneous explosions of saturated solutions of azides during crystallization

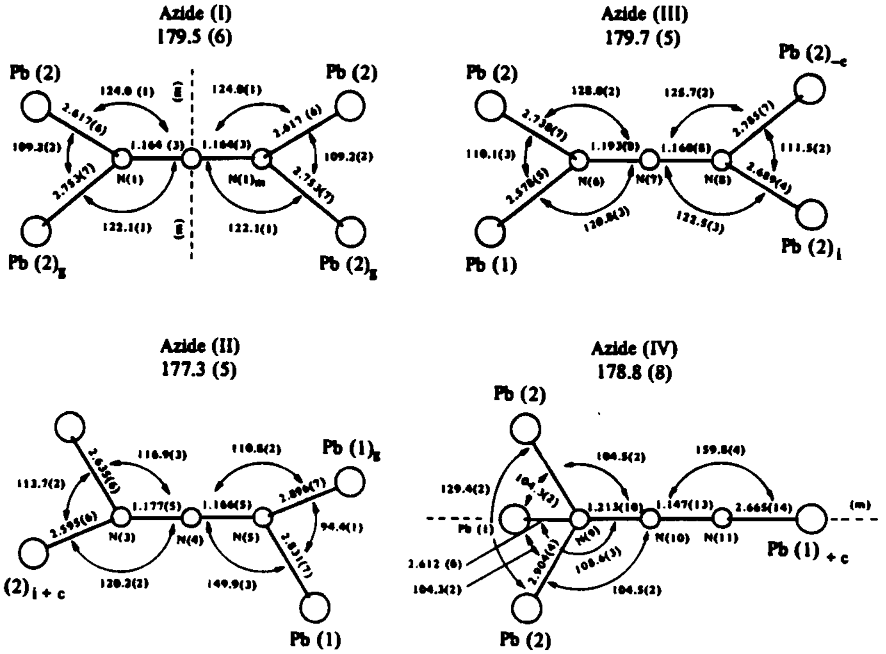


FIG. 79. Four crystalline forms of α-lead azide, according to Choi and Boutin [114].

have been described. Spontaneous explosions were described for cadmium [45], cupric and mercuric [96], lead [91, 96, 97, 98] azides. Rogers [99] gave a description of his experiments with lead azides and Taylor and Thomas [100] thoroughly examined the conditions of the experiments. They prepared a 0.7% lead azide solution in 50 cm^3 of hot 5% aqueous ammonium acetate and allowed it to cool to room temperature. After 11,400 sec (i.e. 1800 sec before the expected time of explosion) the crystallized out large crystals were filtered out and the liquid was left to stand. At the expected time a major explosion of the liquid occurred, but the filtered crystals remained intact. The authors tried to rationalize the phenomenon in terms of formation of nuclei and electric discharge of different layers of nuclei.

Fox, Jenkins and Taylor [101] discussed the three hypotheses which materialized to explain the phenomenon of spontaneous explosions, these are:

(1) the release of stored energy which is high enough to cause an explosion [97],
(2) reactive intermediates were formed in the solution [98],
(3) discharge of sparks between growing crystals [100].

The third hypothesis seems at present to be the most probable. To verify it, Fox *et al.* [101] placed a metal electrode near the surface of the solution and measured the accumulation of electric charge. Indeed, in the solution in which explosions took place very strong charge fluctuations preceded explosions. Small lead detonators fired by Taylor and Thomas did not induce the explosion of the liquid which emanated from the crystals of lead azide. This indicated that the product – crystals of lead azide – have not yet existed in the solution. Stirring and introducing additives suppressed spontaneous explosions. Stirring dispersed the charges and did not allow their localized accumulation. The additives were absorbed by crystals at an early stage and created a lower spark sensitivity.

Sensitivity of Lead Azide

Sensitivity to high temperature was extensively studied [124]. Chaudhri and Field [127] recently described a dependence on temperature of initiation of α-lead azide on crystal thickness, while studying individual single crystals of known size. There was a drop in the explosion temperature from 415 to 385°C for an increase in crystal thickness from 4 to 30 μm. Crystals of less than 3 μm thickness did not explode even up to 450°C. They did not melt at this temperature.

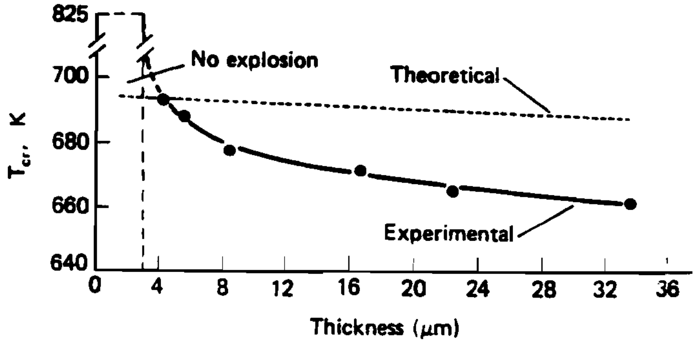


FIG. 80. Critical explosion temperature against crystal thickness, according to Chaudhri and Field in [3, Vol. I, p. 383].

In vacuo no critical size of crystals was observed [128]. The previously mentioned behaviour of primary explosives at high *vacuo* [39–45] may explain the failure to find the critical size of lead azide under very low pressure.

As has been mentioned large crystals of lead azide are more sensitive to impact than the small ones [124]. This was noticed by Solonina as early as 1910 [1].

Direct flame (e.g. from black powder), sparks of electric discharge and glowing electric wires do not readily ignite lead azide and Claessen [129] suggested adding lead styphnate to increase its ease of ignition.

Lead azide is less sensitive to impact than mercury fulminate, as reported by Kozlov (according to [1]).

To increase the sensitivity of lead azide to impact, tetrazene was added in German detonators 'Duplex', according to Bagal [1]. Mixtures of 90–93% lead azide and 10–7% tetrazene were used.

Chaudhri and co-workers [190] determined the rate of detonation of single crystals of α-lead azide. Crystals of cross section 2 mm × 2 mm and above detonated at 8000 m/s, and smaller size (*ca.* 1 mm) exploded at 3000 m/s.

Stability and Reactivity of Lead Azide

Roux [130] kept lead azide at 50°C for 25 months, and at 80°C for 15 months and has not noticed any change of properties. Extensive experiments on the stability of lead azide were carried out by Solonina (in 1910) and Bubnov (in 1940) – according to [1]. The following are conclusions based on their work:

(1) Dry lead azide does not react with metal casing made of aluminium and copper or their alloys (brass, duraluminium).
(2) In the presence of carbon dioxide, moist lead azide did not react with aluminium.
(3) In the presence of carbon dioxide or other acidic compounds, moist lead azide can react with copper casing. Hydrazoic acid was evolved which reacted with copper or copper oxides to yield copper azides.

As recently discovered moisture without carbon dioxide can also promote reactions of lead azide.

As known copper azides are sensitive IE and considerable work has been done to protect metals from reaction with lead azide.

The Manufacture of Lead Azide (Vol. III, p. 178)

The description below is based on information from [1] and [3 (Vol. 2)].

'Colloidal' lead azide. This is a pure form of lead azide (over 99% purity) in fine particles of 3–4 μm. It is non-hygroscopic but not readily pourable and hence less adaptable for mass production. It is particularly sensitive to electric discharge and hence used for electric detonators. For this purpose 'colloidal' lead azide is often mixed with a concentrated nitrocellulose solution in ethyl ether–ethanol or other solvents.

Colloidal lead azide is obtained by adding at 25°C 4% aqueous solution of sodium azide to a small excess of lead nitrate solution. The precipitate is filtrated and washed with water and dried. Its density under 3000 kg/cm^2 pressure is 2.77 g/cm^3 (as compared with 2.93 g/cm^3 of crystalline lead azide).

British 'Service' lead azide. This is a crystalline lead azide containing a small proportion of lead carbonate on the surface of crystals. It is obtained by adding

1 M lead acetate and 2 M sodium azide solutions to the reactor which contains a quantity of sodium carbonate solution. The lead acetate is started a little ahead of the sodium azide so that some lead carbonate is formed which serves as a seeding agent for lead azide crystals. It contains 98.1% $Pb(N_3)_2$, crystals are large (*ca.* 55 μm), density under 15,000 kg/cm^2 is 3.31. Its temperature of explosion is 350°C with an induction period of 5 sec. It is non-hydroscopic, contrary to the dextrinated lead azide which is slightly hygroscopic due to the presence of dextrin.

Dextrinated lead azide. Dextrinated lead azide is made by adding, over a period of 30 min at 60°C, a dilute (3%) sodium azide to an equal volume of a lead acetate solution (7%) which contains dextrin from potato starch in a quantity of 6% to the expected yield of 6% of lead azide. The dextrin solution is made slightly alkaline with sodium hydroxide. The product contains *ca.* 92% of lead azide.

According to [3 (Vol. 2)] in Sweden a temperature of 75°C is maintained during the reaction, and du Pont Co. introduced 0.25% calcium stearate as an agent for coating the dextrinated particles. According to [1] the hygroscopicity of dextrinated lead azide can be higher than 0.5%.

British RD 1333 lead azide. The significant feature of this type of lead azide is the presence of sodium carboxymethylcellulose (CMC) without using sodium carbonate.

Here are the salient features of the process: 1.21 sodium CMC solution (10 g NaCMC/litre) were mixed with 0.145 litre of Empilan AQ 100 solution (100 g contains 100% ethylene derivative of lauric acid/litre) made up to volume of 15 litres with water are kept at 25°C. During a period of 60–70 min, introduced simultaneously, the solutions of sodium azide (108 g NaN_3/litre) and lead acetate (315 g $(CH_3COO)_2Pb \cdot 3H_2O$/litre) – 14 litres of each while stirring. The product precipitated and is washed by decantation, filtered and dried. The yield was 3.3–3.3 kg lead azide. The content of $Pb(N_3)_2$ 96.3%.

According to the U.S. experiments the temperature of the reaction 30–35°C should be maintained. The quantity of CMC is a critical parameter. The product should have a right viscosity and the degree of etherification. The rate of stirring should not be below a certain norm (e.g. 200 rpm).

British RD 1343 lead azide. This is almost identical with RD 1333 except that the wetting agent is omitted and the sodium azide is made more alkaline. It did not cause a deposit to build up a water line in the reaction kettle, leading to reduced cleaning operation.

Special Purpose Lead Azide (SPLA) [(3 (Vol. 2, p. 44)]. The Special Purpose lead azide was introduced in the U.S.A. It is of a greater sensitivity and lower hygroscopicity than dextrinated lead azide. It does not differ much from RD 1333 preparation. The difference is in temperature 37 ± 2°C and faster introduction of reagents (30 min).

Polyvinyl Alcohol Lead Azide (PVA Lead Azide). Polyvinyl alcohol was used instead of dextrin in Germany [2]. In the U.S.A. it is in use in Olin Mathson Corporation [131]. The addition of 3% PVA makes lead azide of better initiating properties, higher density and an easier inflammability than dextrinated lead azide [1].

Gelatine Lead Azide (GAM). Animal gelatine was used for crystal modification of lead azide with the addition of a small amount of molybdenum sulphate [132]. It is claimed that the product is safer in handling than usual lead azide.

Spheroidal dextrinated lead azide. In the 1950s a spheroidal form of dextrinated lead azide was developed by Taylor and co-workers [185] and was named RD 1352. The method was tried in the U.S.A. and described in [3, (Vol. 2, p. 32)].

It consists essentially in reacting aqueous solutions of sodium azide and lead azide in the presence of solutions of dextrin and Tamol SN (surface active agent) at 60°C with an agitator revolving at 275 rpm. After cooling, the mother liquor was decanted, the precipitate washed with water, alcohol and dried.

The picture of the product by this interesting method is given in Fig. 81 (b, c). For comparison British Service lead azide (a) is also given.

SILVER AZIDE (Vol. III, p. 182)

A correction should be made to the description in Vol. III of some properties of silver azide: it is non-hygroscopic, according to C. A. Taylor and Rinkenbach [133] and Costain [3, (Vol. 2, p. 51)]. The hygroscopicity described previously was probably due to impurities.

The photosensitivity was discussed in Volume III.

Silver azide is soluble in ammonia to form a complex, upon evaporation of ammonia the azide is recovered unchanged. In nitric acid it dissolves with decomposition and the evolution of HN_3. On exposure to light silver azide turns first violet and finally black, as colloidal silver is formed and nitrogen evolved [3 (Vol. 1, p. 58)].

A suspension of silver azide in boiling water decomposes with colouration similar to that of the photodecomposition [91]. When heat-dried the azide turns violet at 150°C, and melts at 251°C to a dark liquid. At 253°C it starts evolving nitrogen and metallic silver. When heated rapidly it explodes at 300°C emitting a green light [91, 3 (Vol. 1, p. 58)].

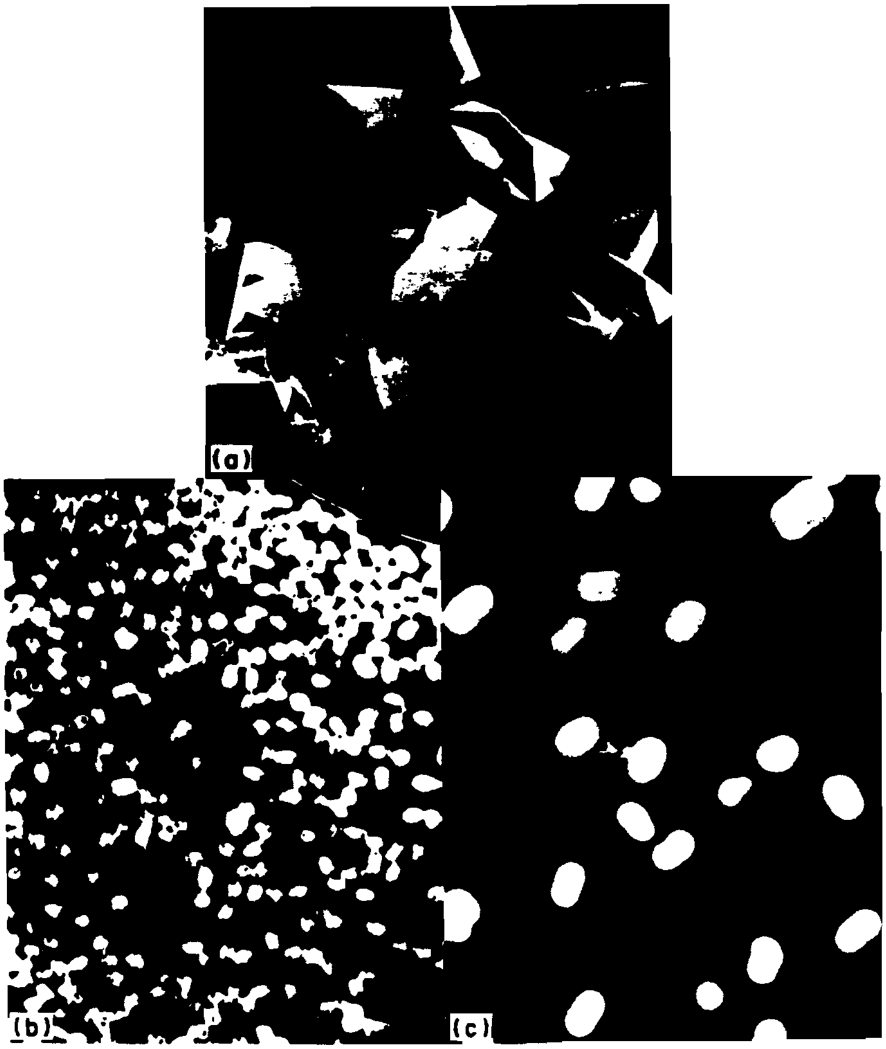


FIG. 81. British Service 170x (a)* and Spheroidal Dextrinated Lead Azide (Picatinny Arsenal) x 50: (b) 20 min and (c) 30 min respectively after start [3, Vol. II].
*British Crown copyright reserved.

Silver azide crystallizes in an orthorhombic form with four molecules per unit cell. This was established by a number of authors [134–137]. The unit cell has dimensions of: $a = 5.6170, b = 5.9146, c = 6.0057$.

It has better initiating property than lead azide (Vol. III, p. 177).

Silver azide is now in use in small and strong detonators in the U.K., U.S.A., Holland, Sweden and Germany. The main obstacle against the use was originally the fact that silver azide was not in a suitable form for pouring and pressing into detonators. During the early 1950s G. W. C. Taylor [138], Williams and Peyton [139] developed processes for making granular AgN_3.

The method used in Picatinny Arsenal [2] is as follows. The reaction was carried out in a 10-litre stainless steel kettle with a stirrer. The reagents were: 2.0 l of filtered 2N silver nitrate solution, 2.0 l of filtered 2N sodium azide solution, 1.07 l of filtered pure ammonia (28%) solution. Silver nitrate followed by ammonia was introduced into the reaction kettle. Under vigorous mixing sodium azide solution was introduced and the content was warmed to 75°C within 5 min. Silver azide started to precipitate *ca.* 5 min later.

At this point 50 ml of acetic acid 3N solution was added over 5 min to induce seed-crystal formation. Distilled water was added at a rate of 40–60 ml/min to maintain the original level and avoid evaporation losses.

When the total time at 75°C was 30 min, heating was increased to reach 97°C within 10 min and over the next 60 min the temperature was raised to boiling point which indicated that all the ammonia had boiled off. Cold water (3.5 l) was added and brought into the jacket to cool the content of the vessel. During the cooling, 50 ml of 3N acetic acid was introduced into the kettle. After 10 min the temperature reached 30°C, the stirring was stopped, silver azide was allowed to settle and the solution was decanted. The product was decanted with two portions of 3 l distilled water. The product was collected on a cloth-filter, washed with ethanol (95%) and dried for 40 hours at 50°C. The yield was 540 g (90%).

Vigorous stirring during the evaporation of the content of the vessel is very critical. Without stirring large flat crystals are produced. The quantity of acetic acid added for seeding was important for achieving uniform bulk density.

Cadmium Azide $Cd(N_3)_2$

Cadmium azide was obtained by Curtius and Rissom [200] and Bassière [95]. Some work has been dedicated to its properties (Vol. III, p. 186).

According to Bowden and Singh [201] it is not decomposed by α- and γ-radiation. It shows the rate of detonation 4200 m/s. According to Wöhler and Martin [202] it is less sensitive to impact than lead azide, but more sensitive than silver azide.

Storage of Azides

Experiments on the storage of lead azide have shown [3 (Vol. 2)] that different types of lead azide withstand long storage. Some samples taken after 25 years of storage under standard storage conditions did not show any deterioration.

Toxicity

All azides are toxic, but their toxicity is due to the evolution of hydrazoic acid. The solid, insoluble azides such as lead and silver azides are practically non-toxic. Considerable studies were dedicated to the toxicity of sodium azide. It was found that the minimum lethal dose of NaN_3 is 35–38 mg/kg body weight [140]. Chronic poisoning with NaN_3 was studied by Bassendowska and co-workers [141]. They showed that the maximum permitable concentration of NaN_3 in air is 2 mg/m^3, provided the skin of the worker is well protected.

Destruction of Lead Azide

Lead azide can be destroyed by acting with sodium hydroxide 10% solution at 20°C which gives $Pb(OH)_2$ and aqueous solution of NaN_3: (method of Kramer) [3 (Vol. 2, pp. 85–86)]:

$$Pb(N_3)_2 + 2\,NaOH \longrightarrow Pb(OH)_2 + 2NaN_3. \tag{11}$$

Sodium azide can be recovered by evaporation and crystallization.

Another method was suggested by Richter [3 (Vol. 2)]. It consists in using a more concentrated (20%) sodium hydroxide:

$$Pb(N_3)_2 + 4\,NaOH \longrightarrow Na_2PbO_2 + 2\,NaN_3. \tag{12}$$

Here lead compound remains in solution in the form of sodium plumbate. Careful acidification of the solution with nitric acid leads to the formation of lead azide.

Data for lead azide [142] (Vol. III, p. 172)

Enthalpy of formation	+391.3 kcal/kg
Volume of detonation gases	231 l/kg
Density	4.8 g/cm^3
Deflagration point	320–360°C
Lead block test	110 cm^3
Impact sensitivity:	
pure product	0.25–0.40 kpm
dextrinated	0.3–0.65 kpm
Specification (U.S.A.).	
Net content (by determination as $PbCrO_4$)	min. 91.5%
Moisture	max 0.3%
Mechanical impurities	nil
Water solubles	max 1%
Lead content	min. 68%
Copper content	nil
Reaction	neutral

Bulk density	min. 1.1
Deflagration point not below	300°C

Lead azide detonators for coal mining have copper tubes. For all other blasting aluminium caps are used.

MANUFACTURE OF SODIUM AZIDE

It is appropriate to give a description of the basic compound used for producing azides. Below is a short description based on that of Bagal [1].

As known this is a two-step reaction (13):

$$Na + NH_3 \longrightarrow NaNH_2 + \tfrac{1}{2} H_2 - 21 \text{ kcal} \qquad \textbf{(13a)}$$

$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O. \qquad \textbf{(13b)}$$

(a) Sodamide (Fig. 82)

Sodium should be of 99.5% purity. Gaseous ammonia – in a steel bottle (1) warmed to 30°C – should not contain more than 1% water. It is dried over

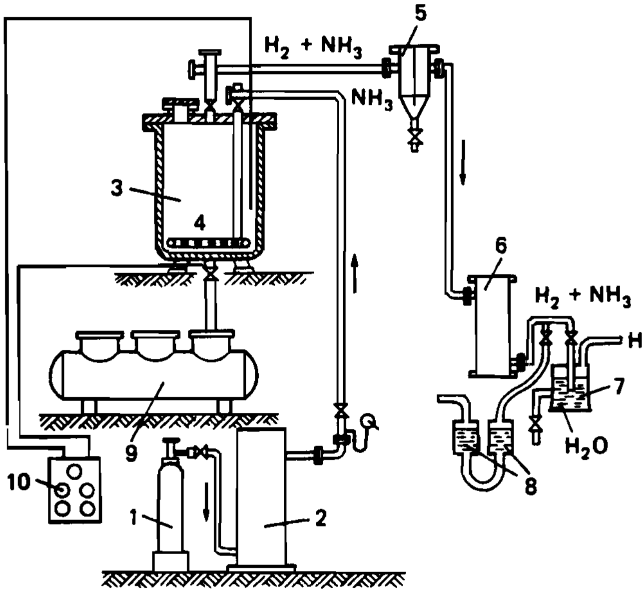


FIG. 82. Amidation of Sodium, according to Bagal [1] 1 – ammonia steel bottle, 2 – drying column, 3 – reactor, 4 – perforated ring, 5 – dephlegmator, 6 – safety column, 7 – water container, 8 – flowmeter, 9 – sodium azide reactor, 10 – controls.

NaOH and KOH in (2) before entering the 200 l reactor (3) made of stainless steel with an air-tight cover and a stirrer with 100 revolutions/min. It should be warmed to 150–200°C, washed inside for 5–10 min with gaseous ammonia and loaded with 28 kg of sodium. The reactor is heated to 360°C and ammonia introduced (4). At the beginning a temperature of 380°C is maintained. When the gases leaving the reactor contain 80% hydrogen, the temperature should be lowered to 340–350°C, as a higher temperature may produce a distillation of sodamide which would cause deposits to form in the gas conduction pipes. The end of the reaction is manifested by the fall of hydrogen content to 2–8%. One batch of sodamide consumes 35–40 kg of ammonia. The yield of sodamide was not given.

The gases from the reactor are passed through the dephlegmator (5) and safety column (6) which prevents a return of gases to the reactor. Finally the gases enter water container (7) and retain out flowing ammonia.

It is important not to introduce ammonia after the process has ended, as it can form undesirable impurities (an 'over amidation').

(b) Sodium Azide (Fig. 83)

The reaction is carried out in a horizontal heated electrical apparatus made of steel. Before starting the reaction it should be thoroughly dried by warming to 170–200°C. To check the tightness of the apparatus ammonia is blown through for 5–10 min. Hot melted sodamide (350°C) is poured from the amide apparatus. The reaction of sodamide with nitrous oxide is exothermic and there is little need of heating the reactor. The best temperature of the reaction is 200–220°C. At 250°C the reaction is too fast and may lead to an explosion. To achieve the uniformity of the reaction nitrous oxide is introduced into both ends of the reactor.

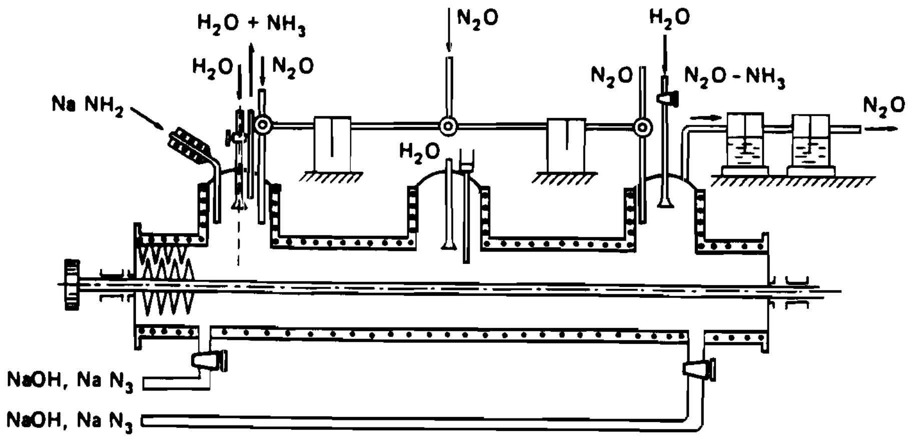


FIG. 83. Reactor for production of sodium azide, according to Bagal [1].

An analysis of out going gases should be carried out. They should contain 35–40% N_2O and 25–30% NH_3. The end of the reaction is manifested by the fall in the ammonia content to 3–5% NH_3 and the fall of temperature. The time to carry out the reaction of one batch is *ca.* 30 hours and the yield is 28–30 kg.

The content of the reactor is cooled to 100°C and washed with water. Care should be taken with this process, as water reacts vigorously (exothermic reaction) with unreacted sodamide. Sodium azide with sodium hydroxide is taken by water (200 l), filtered and evaporated to a density of 1.55–1.57 at 20°C. Sodium azide is collected, washed with a small quantity of water and finally with ethanol.

Sodium Azide Formation in Liquid Ammonia

This method was worked out in the U.S.S.R. [1] and based on a reaction at relatively low temperature in liquid ammonia. Both reactions: amidation and azidation can be carried out in the same reactor – autoclave of 200 l capacity and pressure up to 100 kg/cm^2.

Liquid ammonia dissolved sodium and the solution (under the action of catalysts) reacted to form sodamide. Sodamide is practically insoluble (*ca.* 0.1%) in liquid ammonia and precipitated as a fine powder. The catalyst is ferric oxide in quantity 3–5% (relative to sodium). The reaction takes 30 min to 1 hour at *ca.* 50°C. Hydrogen escapes from the autoclave at 40–60 kg/cm^2 through a safety valve working at this pressure.

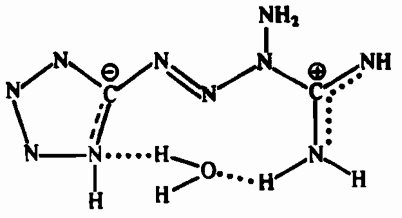
The suspension of sodamide in liquid ammonia can readily react with nitrous oxide. Nitrous oxide kept in steel bottles under pressure is introduced into the autoclave under 25 kg/cm^2 maintaining the reaction temperature of 50°C.

The reaction of N_2O with $NaNH_2$ in liquid ammonia is a somewhat complicated reaction. At first the reaction forms a complex 2 $NaNH_2$, N_2O. In the presence of an excess of ammonia over 0°C sodium azide is formed. However in the presence of sodium hydroxide the basic sodium azide ($NaN_3.2NaOH$) results. A higher temperature (e.g. 30–50°C) favours the formation of the basic compound, while a temperature of *ca.* 0°C prevents the formation of this substance.

Finally, a good solubility of sodium azide and practically no solubility of sodium hydroxide in liquid ammonia makes the separation of sodium azide from sodium hydroxide possible. Sodium azide retained on a filter should be washed with liquid ammonia. After ammonia has been evaporated, pure sodium azide remains with a yield of 99%.

TETRAZENE (TETRACENE) (Vol. III, p. 206)

Relatively recent X-ray analysis by Duke [147] confirmed the structure given by Patinkin, Horowitz and Lieber (formula I, Vol. III, p. 207). This is depicted by formula (XII) where the substance is presented as a zwitterion of 1-amino-1-(1H-tetrazol-5-yl)azo guanidine hydrate.



XII

The heat of explosion is 558 kcal/kg and heat of formation $-H_f = -70$ kcal/mol.

The following properties are according to the U.S. Military Specification [148]:

Colour and appearance	white to light yellow coloured needle shaped crystals
m.p. and explosion	130 ± 2°C
Granulation	100% should pass through No 45 sieve
Specific gravity	1.65 ± 0.05
Heavy metals	absent

Meyer [142] gives some additional requirements:

moisture	max. 0.3%
aqueous extract	no acid present (on universal paper)
pouring density	0.3
deflagration point	min. 138°C
lead block test	155 cm^3

It is slightly more sensitive to impact than mercuric fulminate.

Bubnov (according to [1]) gave the figures of density depending on the pressure applied:

pressure	100	200	300	400	500	600	1000	1600
density	1.052	1.179	1.289	1.304	1.377	1.401	1.493	1.503

Pouring density was given as 0.45.

It is non-hygroscopic: at 30°C and relative humidity 90% it absorbed 0.77% water. It does not attack metals at room temperature [149], and does not react with concentrated ammonia at room temperature, sodium and potassium hydroxides decompose the substance and ammonia is evolved.

With concentrated acid it forms salts: hydroxide, perchlorate, sulphate nitrate. They are all explosive and their initiation temperature is *ca.* 140°C.

The practical use is limited to detonators which are initiated by another primary explosive and tetrazene is used as an intermediate booster or when mixed with another primary explosive to increase its sensitivity to flame or spark. The mixture tetrazene was used in explosive rivets (Vol. III, p. 240). Dynamit A.G. patented [150] mixtures of tetrazene with lead azide for this purpose.

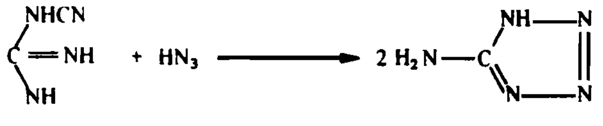
A few initiating compositions with tetrazene have been described in the Encyclopedia [148]. The most important seems to be 'Sinonydsatz' developed in Germany as a replacement for mercury fulminate mixtures. It proved to be non-corrosive and did not erode barrels of firearms. Their composition was: lead styphnate 25–55, tetrazene 1.2–5.0, barium nitrate 25–45, lead dioxide 5–10, anthymony sulphide 0–10, calcium silicide 3–15, powdered glass 0–5%.

Duplex-Cap (detonators) contained 0.3 g of a mixture of lead azide (92.5%) tetrazene (7.5%) pressed at 100 kg/cm² over 0.05 g of unwaxed PETN pressed at 300 kg/cm².

Tetrazole Derivatives and their Salts (Vol. III, p. 210)

Since the advent of Tetrazene attention has been paid to other compounds which contain tetrazole ring. An excellent review on Tetrazoles was given by Herman in the Encyclopedia [190]. Silver and mercury salts of 5-nitrotetrazol were suggested in Germany during World War II to replace the fulminates. According to the same source [190] mercuric salt of 5-nitrotetrazol proved to be a powerful initiating explosive. It is sensitive to friction, has an explosion temperature of 210°C. It seems that it is too sensitive for practical use.

The chemistry of tetrazol derivatives was reviewed by Bensen [192]. The simplest and most versatile derivative is 5-aminotetrazol (Vol. III, p. 210). It is usually obtained by the method of Stolle and Schick [151] from cyanoguanidine and sodium azide in an acid medium:

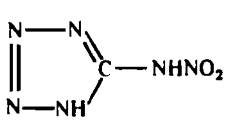


(14)

XIII

m.p. 203°C

Nitramino derivative of 5-aminotetrazol (XIV)

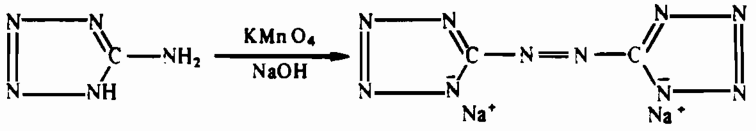


XIV

was claimed [152] to yield a lead salt with initiating properties. The *N*-nitro compound (XIV) was described by Lieber *et al.* [153].

Azotetrazol

According to Thiele [154] oxidation of 5-aminotetrazol with potassium permanganate in the presence of an excess of sodium hydroxide yielded sodium salt of azotetrazol:



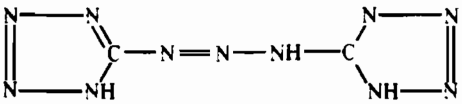
XV Sodium salt

Basic lead salt of azotetrazol (bulk formula $C_2H_{10}Pb \cdot 5H_2O$) was used in Germany during World War II. A description of the method of manufacture according to Bagal [1] is given here. The starting substance was sodium salt of 5-aminotetrazol (XIII). The sodium salt dissolved in a solution of sodium hydroxide at 70–80°C was charged with a 25% excess of potassium permanganate at the rate which would maintain the temperature 95–100°C. The solution should be brown. The filtered solution was cooled, the precipitated sodium salt was collected and dried at a temperature below 30°C.

To obtain the basic lead salt a solution of 3% sodium salt of XV containing 0.775% NaOH was prepared. The solution was poured into 7.5% solution of lead nitrate in a tilted reactor at 43–44°C. The precipitated basic lead salt was collected, washed with water of 30–30°C, ethanol and kept as ethanol moistened product. The yield was a 78% based sodium salt of XV.

The salt was used for electric igniters. The substance was mixed with nitrocellulose varnish and fixed on the resistance bridge.

Another important derivative of tetrazol is 1,3-ditetrazyltriazine (XVI)

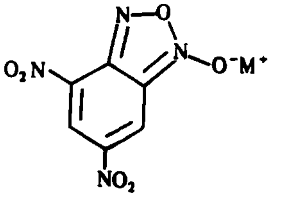


XVI

This was obtained by K. A. Hofmann and Hock [155] as described in Vol. III, p. 210. The compound forms colourless thin plates, crystallizing with 1 mole of water. It has masked acidic properties and can readily form salts with metals. On boiling with dilute hydrochloric acid it yielded 5-aminotetrazol (XIII) and nitrogen. The compound was described in review [156]. Sinha, K. R. K. Rao and Sankaran [157] made an extensive study of the properties of the substance and its salts. Lead salt has an explosion temperature of 185°C. Bahadur [158] described lead double salt of XVI and styphnic acid as an initiator. Practical experiments have shown that the salt is too dangerous to handle.

FUROXANE DERIVATIVES

Attention was recently drawn to the initiating properties of some salts of nitro derivatives of benzofuroxane. Potassium and barium salts of 4,6-dinitrobenzofuroxane as primary explosives were suggested by Piechowicz [193]:



No information is available as to the practical application of this salt.

The potassium salt was described as early as in 1899 by Drost [194], and a number of authors [195, 196] mentioned explosive properties of the salts of the above compound.

Benzofuroxane can be obtained according to Green and Rowe [195] by oxidation of *o*-nitroaniline with sodium hypochlorite. Nitration of benzofuroxane at 5–20°C yielded 4,6-dinitrofuroxane [194–196].

An excellent review on furoxanes was given by Kaufman and Picard [197].

Pepekin, Apin and co-workers [203] determined the energy of dissociation of the bond $N \rightarrow O$ in benzofuroxane. They found a value of 59.5 kcal/mol.

NITRO DERIVATIVES OF PHENOLS (Vol. III, p. 212)

An experimental work on thermal decomposition of the salts of picric and styphnic acids has been carried out by Andreev and Lu-Bao-Fen [159]. Ammonium, potassium and lead salts were examined, and the results summarized in Table 75.

The curve: rate of decomposition/temperature shows an autocatalytic trend of reactions.

The decomposition of styphnates occurs at a lower temperature than that of picrates.

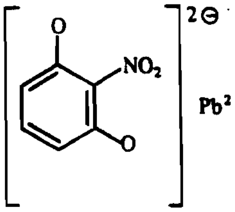
Lead Mononitroresorcinol (LMNR)

The lead salt of mononitroresorcinol was in use in electric detonators for making fuseheads. Some of them may be composed of this salt and dextrinated lead azide [159, 160].

The main problem in making LMNR is the use of 2-mononitroresorcinol

TABLE 75. Thermal decomposition of picrates and styphnates

Salt	Interval of temperature res °C	E kcal/mol	Half-life time at 230°C, minutes
Potassium picrate	250–300	41.2	8600
Lead picrate	230–260	60.2	920 explosion at 260°C
Hydrogen Potassium Styphnate	170–200	47.6	262 explosion at 200°C
Di-potassium Styphnate	200–240	51.7	210 explosion at 250°C
Lead Styphnate	200–230	36.4	143 explosion at 240°C



XVII

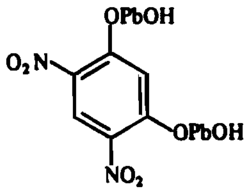
which should be obtained by very careful nitration of resorcinol. Resorcinol is heated with fuming sulphuric acid at 100°C for 30 min. The solution is cooled to 25°C. After adding mixed acids it is allowed to stand for 30 min. The addition of water follows and distillation of the product with steam. It forms orange coloured prisms, m.p. 84–88°C, boiling p. 232–234°C [161, 162a].

Lead 2,4-Dinitroresorcinate (Vol. III, p. 220)

The Encyclopedia of Fedoroff and Sheffield [162b] gives some figures on the properties of lead dinitroresorcinate. It explodes at 265°C (induction 5 sec), heat of explosion is 270 kcal/kg. It is slightly hygroscopic: at 30°C, 90% relative hygroscopicity is 0.73%. It has low initiating property: 0.4 g did not initiate tetryl pressed at 70 kg/cm^2.

Basic Lead 4,6-Dinitroresorcinol

The salt was developed in Great Britain during World War II [162c]. Finely ground (40 g) resorcinol was gradually introduced to 98% nitric acid (400 g) at −15° to −20°C. The low temperature was kept by adding solid carbon dioxide to the nitration vessel. After all the resorcinol was introduced, the nitra-



XVIII

tion mixture was cooled to −50°C and then drawn into 5 times its volume of water with ice.

The crude product was purified by dissolving in 5% NaOH solution and pouring the solution into hot boiling 12% sulphuric acid. The precipitated dinitroresorcinol was washed with water. The yield was 27.5 g, that is, *ca.* 40% of theoretical.

The product reacted with an excess of freshly precipitated lead hydroxide suspended in water at 90°C.

According to existing information [162c] large scale manufacture of the salt in Great Britain was carried out by reacting dinitroresorcinol freshly filtered from nitric without purification with lead hydroxide at 90°C.

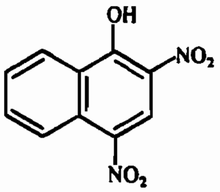
Lead Styphnate (Vol. III, p. 213)

No relevant facts can be added to those reported previously. The following are data taken from Meyer's textbook [142]:

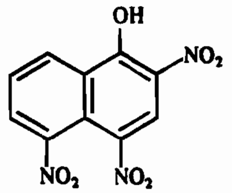
density	3.0
deflagration point	275–280°C
heat of explosion	370 kcal/kg
lead block test	130 cm^3 (according to [162d])
(it is 40% of TNT or 39% of picric acid).	
detonation velocity	4900–5200 m/s
Specification	
net content	min. 98%
moisture	max. 0.15%
lead content	
(determined as $PbCrO_4$)	43.2–44.3%
Heavy metals other than lead	max. 0.05%
Ca and Mg	max. 0.5%
Na	max. 0.07%
pH	5–7
nitrogen content	min. 8.8%
bulk density	1.3–1.5
deflagration point	min. 270°C

Lead Salts of Nitronaphthols

Recently Japanese authors [163] suggested the use of lead salts of di- and trinitro-α-naphthol, for example XIX and XX:



XIX



XX

According to the authors the salts are less sensitive to heat, impact, friction and electric discharge than the corresponding salts of phenol and resorcinol.

Complex Salts (Vol. III, p. 230)

In addition to complex perchlorates (Vol. III) Ni, Co and Cd form the following complex salts with hydrazine nitrate:

Ni $(N_2H_4)_3(NO_3)_2$ – deflagration at 215°C
Co $(N_2H_4)_3(NO_3)_2$ – deflagration at 210°C
Cd $(N_2H_4)_3(NO_3)_2$ – deflagration at 245°C

According to Médard and Barlot [164] they could be recommended as primary compounds. They possess the advantage that they are less sensitive to impact than mercury fulminate and lead azide. Their disadvantage is that they are difficult to ignite.

Nickel salt was examined in detail. It expands in lead block of *ca.* 85% of picric acid. The velocity of detonation in an 8 mm diameter plastic tube was found to be 2900–3100 m/s.

1,3,5-Triazido-2,4,6-Trinitrobenzene (Vol. III, p. 193, formula IX)

The substance is readily transformed into benzotrisfuroxane (Vol. I, pp. 603–604, formula II and Vol. III, p. 193, formula X). Kinetics of the transformation was studied by Korsunskii and Apina [181] – see Chapter IV.

Dinitrobenzenediazooxide (Dinitrodiazophenol DDNP, DINOL)
(Vol. III, p. 201)

Little can be added to the information given in Vol. III. According to Fordham [183] it has a velocity of detonation of 6900 m/s at a density of 1.58. As compared with other initiating explosives it is relatively insensitive to impact and friction. It has good storage properties and an application has been found in both commercial and military detonators, particularly in the U.S.A.

Salts of Acetylene (Vol. III, p. 227)

Silver acetylide. Although silver acetylide has not received practical application it has been the subject of a few published papers. Stettbacher [165] was first to draw attention to the very strong initiating properties of silver acetylide. He found that the initiating charge is 0.07 g (for AgN_3 and mercuric fulminate he found figures of 0.02 g and 0.29 g respectively).

Tamman and Kröger [166] compared the properties of the acetylide and the double salt $Ag_2C_2 \cdot AgNO_3$. The latter was obtained by acting with acetylene on a solution of $AgNO_3$ in dilute nitric acid. The initiation temperature was found to be 202–207°C (depending on the rate of heating). Silver acetylide gave figures of 143–148°C. A wide description of the properties of the double salt $Ag_2C_2 \cdot Ag\ NO_3$ was given by Stadler [167]. It was obtained by introducing acetylene into a solution of 50 g $AgNO_3$ in 200 cm^3 water and 30 cm^3 nitric acid (d 1.4) at 80–90°C. The velocity of detonation was 2250 m/s and 4450 m/s at densities of 2.51 and 5.36 respectively. The lead block expansion was 136 cm^3. The heat of explosion for the double salt was 183 kcal/mol (for silver acetylide 70.3 kcal/mol).

MANUFACTURE OF PRIMERS

One of the leading explosives factories in Europe, Vihtavuori Works in Finland, has developed a modern process for the manufacture of primers after the explosion in 1961 [180]. The main novelty being remote control.

The building for the manufacture of primers has a corridor running through the middle and on both sides of the corridor are steel–concrete chambers. The outer walls of the chambers are lightly built. In the corridor walls, part of the concrete is replaced by 30 mm steel plate, to simplify the fixing of the control apparatus. The explosives – lead styphnates, lead azide and tetrazene are kept and transported from one stage to another in 1 kg canisters. They are grasped with tongs and transported from one chamber to another by trolleys moved by a cable. Steel trapdoors in the dividing walls are opened and closed by remote control.

Lead styphnate and lead azide are precipitated in correct proportion and mixed by a continuous process.

The five production operations: precipitation, mixing, filtration, drying and sieving are carried out in one chamber. Drying is carried out in the filtration apparatus by washing with solvents and drying with warm air. The explosive is transferred from one apparatus to another by tongs and levers fitted through the armour plating.

The explosive taken into canisters is transferred to another chamber where it is pressed into the proper metal elements.

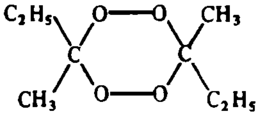
PEROXIDES (Vol. III, pp. 225, 299)

Peroxides as explosives have no practical application with the exception of concentrated hydrogen peroxide, containing over 80% and 90% H_2O_2 (Vol. III, p. 299) as an oxidant in rocket fuel. It also became an important oxidant with a wide application – among reactions with concentrated hydrogen peroxide the reaction $NH_2 \longrightarrow NO_2$ was achieved to obtain hexanitrobenzene (Chapter VI). The reactions of radical polymerization under the catalytic action of acyl and ketone peroxides are well known. Among the latter use has been found for propione peroxide and peroxyacetic acid became a most important epoxidation agent.

A number of monographs and reviews have been published on peroxides in addition to those mentioned in Vol. III (p. 227) [168–176, 168–175]. The problems of peroxide reactions is outside the scope of the present book and only those related to explosives will be described here.

Some peroxides, such as BaO_2, SrO_2 are in use in pyrotechnical compositions [176]. This is outside the scope of the present book.

Propione Peroxide (XXI)

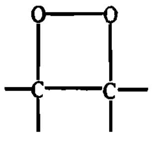


XXI

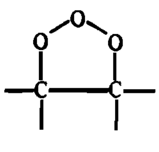
found a wide application as an initiator of radical polymerization. It is much less sensitive to impact and friction than acetone peroxide (Vol. III, p. 225).

Hexamethylenediamine peroxide which has two assigned formulae (Vol. III, p. 225, formulae I and II) was examined with NMR technique by T. Urbański [174], who found that formula I by Baeyer and Villiger [177] was the correct one.

Among peroxides with explosive properties are those from 1,2-diketones (XXII) [178]. They were prepared by ozonolysis or by the action of singlet oxygene on alkanes, or by sodium hydroxide action on bromoperoxide



XXII



XXIII

They possess marked explosive properties. The kinetics of decomposition of ozonides (XXIII) was followed by Mile and co-workers [179].

Superoxides

The name 'superoxide' was introduced in 1934 to signify an exceptional degree of reactivity of superoxide radical anion O_2^- in KO_2 [187]. It was obtained by acting with dioxygen on metals such as potassium (and Rb, C_5). It is marked by nucleophilicity. In aprotic media it reacts rapidly with primary and secondary alkyl halides to yield dialkyl peroxide and with acyl chlorides to yield diacyl peroxides. Superoxides are reduced to peroxides under some experimental conditions. They were recently reviewed by Sawyer and Valentine [188]. No explosive properties of metal superoxides or their mixtures have been recorded.

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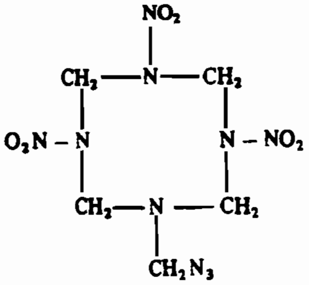
APPENDIX TO CHAPTERS XIII AND XVII

An interesting ***organic azide*** related to octogene (HMX) was recently described by Frankel and Woolery [204].



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CHAPTER 18

BLACK POWDER (GUN POWDER)

(Vol. III, p. 322)

Black powder is still little known as regards the mechanisms of reactions occurring during its burning, although it has been known for more than 2000 years.

Owing to new tools such as differential thermal analysis [1], and advances in solid-state chemistry [2–5], advances in free radical chemistry and ESR technique [6] and catalysis a theoretical and experimental approach to the problems of mechanism was made possible (Vol. III, p. 335).

Concling [7] recently gave an interesting review on burning black powder and pyrotechnic compositions. He presented diagrams of differential analysis of the behaviour of potassium nitrate, sulphur and their mixture when heated. Figure 84 shows a diagram of KNO_3+S mixture.

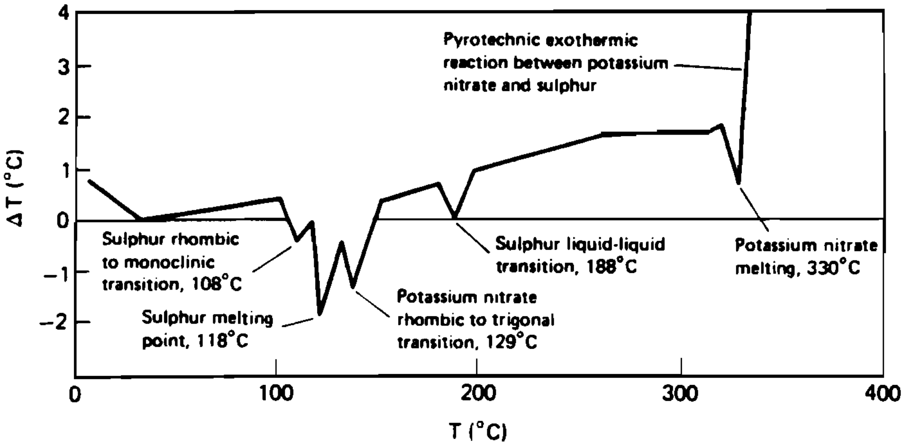


FIG. 84. Differential calorimeter diagram of KNO_3+S according to Concling [7].

One of the problems in burning black powder is: at which moment does the main reaction begin (e.g. Vol. III, p. 338) and whether the reaction occurs in the condensed phase or the gas phase.

Andreev [8] in his monograph pointed out that the burning of black powder occurs mainly in the condensed phase. This explains the experimental facts that the rate of burning depends very little on the pressure and the heat transfer does not go through the gas phase but through the solid or liquid (molten) phase. Also the transformation of the solid phase to liquid occurs through endothermic processes which do not favour the reaction. Glazkova *et al.* [9, 10] systematically examined the deflagration and thermal decomposition of mixtures of potassium nitrate with carbon, sulphur and both these components. Here are her main conclusions:

(1) the rate-controlling reactions of potassium nitrate with charcoal occurred in the condensed phase,

(2) the stoichiometric mixture of sulphur with potassium nitrate indicated that the burning does not depend on density and the rate-controlling reaction occurred in a gas-phase.

The rates of burning of mixtures of potassium nitrate with sulphur are higher than those of potassium nitrate with carbon.

It follows from Fig. 85 on the mixture of three components: KNO_3, carbon and 5% sulphur, that the rate of burning was greater in the samples pressed to the theoretical than to the lower density.

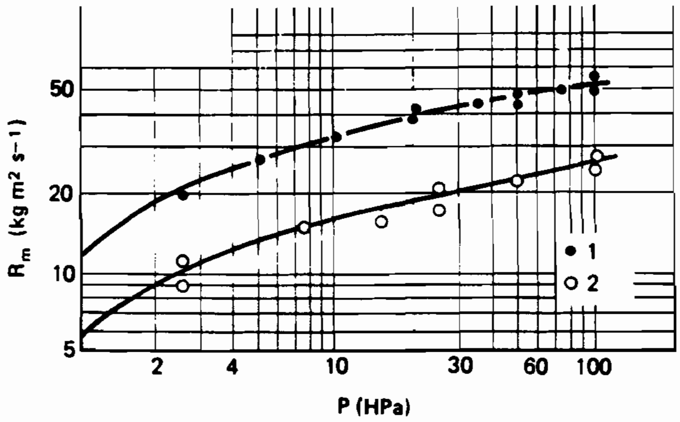


FIG. 85. The rate of burning of a mixture of KNO_3, carbon and 5% sulphur at a lower (1) and higher (2) density, according to Glazkova *et al.* [10].

This meant that the rate-controlling reaction occurs mainly in the condensed phase.

Glazkova also examined the action of catalysts such as lead chromate: it leads to an increase in the importance of reactions in the condensed phase.

Bowden and Blackwood [11] pointed out the important part played by charcoal in the process of burning black powder and the role of soluble constituents present in charcoal.

It is known that unpaired electrons and free radicals are present in charcoal [12]. Also another fact is that the grinding of polymers and charcoal produce the break of covalent bonds $\geqslant C - C \leqslant$ to form free radicals $\geqslant C\cdot$ [13].

T. Urbański advanced the view [14, 15] that free radicals in charcoal considerably influence the properties of black powder. The concentration of free radicals in charcoal depends very much on the temperature of carbonization in the range 245–650°C (Fig. 86). 'Ammonpulver' – a mixture of 85% NH_4NO_3 and 15% charcoal – was prepared from charcoal made at various temperatures of carbonization of cellulose.

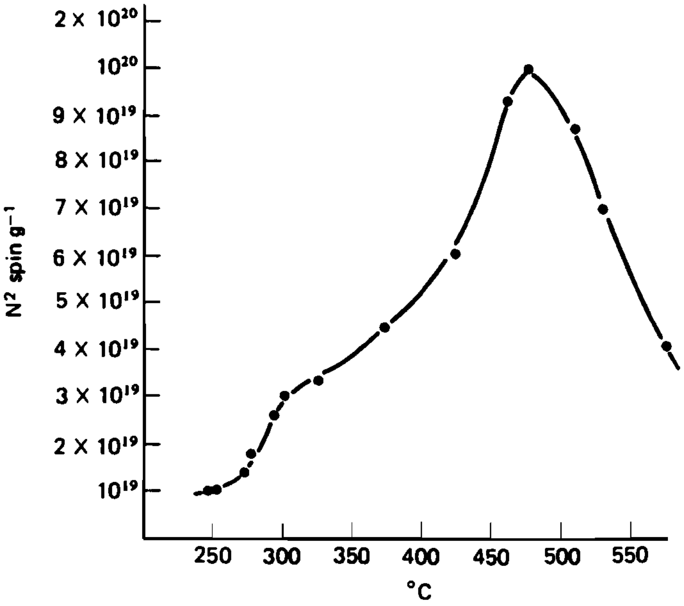


FIG. 86. Spin concentration in charcoal against the temperature of carbonization of cellulose, according to T. Urbański *et al.* [6].

The rate of burning of 'Ammonpulver' was expressed as a coefficient of vivacity determined in a Sarrau-Vieille-Burlot closed vessel [16]. The coefficient of vivacity against temperature of carbonization of cellulose is given in Fig. 88. It follows from the comparison of Figs 86 and 87 that the rate of burning of Ammonpulver has the same trend as the concentration of free radicals in the charcoal. Subsequently it follows that the concentration of unpaired electrons in charcoal is at least one of the factors influencing the rate of burning of black powder.

Modifications of Black Powder

One of the characteristics of black powder is that it is a fast burning mixture.

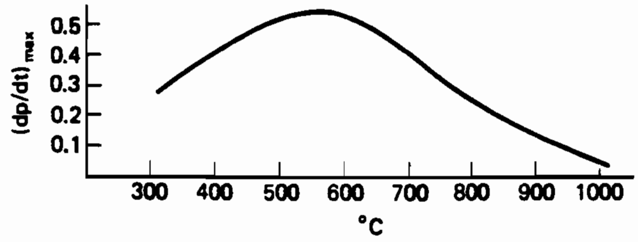
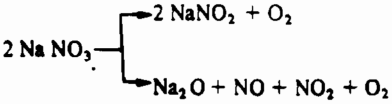


FIG. 87. Rate of burning ('coefficient of vivacity', dp/dt_{max}) of 'Ammon-pulver' against the temperature of carbonization of cellulose, according to T. Urbański *et al.* [6].

Numerous modifications have been introduced, some with the aim of reducing the rate of burning.

One of the modifications consisted in partially (or completely) replacing potassium nitrate by sodium nitrate. Sodium nitrate changed some properties of the mixtures, in spite of the similarity to potassium nitrate. As pointed out previously (Vol. III, p. 329), sodium nitrate mixtures for mining (in Germany 'Sprengsalpeter') gave a better performance than potassium nitrate mixtures (in Germany 'Sprengpulver'). This has never been investigated and explained, but recently a few notes have appeared which point out the difference between sodium and potassium nitrate. Thus according to Towse [17] the difference between these two nitrates can be found in their behaviour at a temperature of *ca.* 900°C. Sodium nitrate decomposed mainly according to equation (1a) but *ca.* 8% reacted in the sense of equation (1b):



$$2\,NaNO_3 \rightarrow 2\,NaNO_2 + O_2 \qquad (1a)$$

$$2\,NaNO_3 \rightarrow Na_2O + NO + NO_2 + O_2 \qquad (1b)$$

Reaction (1b) does not occur with potassium nitrate. In the light of the above it seems that sodium nitrate is more reactive than potassium nitrate at high temperature.

Various modifications of black powder are known. One of the most popular is sulphurless black powder (Vol. III, p. 331). Fedoroff and associates [18] mentioned over twenty different modifications of black powder.

Here are a few modifications introduced with the aim of lowering the rate of burning.

(1) Addition of silicate dust (e.g. brick dust) and graphite. Such mixtures do not burn uniformly and leave a considerable residue.

(2) Addition of resin, which reduces the rate of burning of black powder under atmospheric pressure *ca.* 20 times.

(3) Substitution of pitch for charcoal slows down the burning 4 to 10 times.

(4) Substitution of cuprene (acetylene polyermized on copper as a catalyst) for charcoal.

(5) Introduction of triphenyl phosphate, camphor substituted ureas (as suggested by F. Olsen).

(6) Mixing black powder with nitrocellulose dissolved in a usual solvent, with the ratio black powder/nitrocellulose being 60/40. The resulting dow was extruded in much the same way as cannon propellants. This was known as Benite, developed by Hassmann and improved by Huselton and Kaplowtiz according to [18]. The composition of Benite was: 40% Nitrocellulose (13.15% N), 44.3% KNO_3, 6.3% Sulphur, 9.4% Charcoal. Ethyl Centralite was added to this mixture in a proportion of 0.5%.

According to Stettbacher [19] the addition of 1–6% of $BaSO_4$ is strongly advised to slow down the rate of burning of black powder.

Among recent modifications of black powder a patent [20] should be mentioned. The mixture is composed of potassium perchlorate (60–80%), salts of benzoic acid (40–20%) and a small proportion of water (*ca.* 2%). Water is probably combined with benzoic acid salts in the form of hydrates.

By replacing charcoal with pit (fossil) coal an increase in the rate of burning can occur.

Considerable work is being carried out by Glazkova *et al.* [21, 22] on the burning of mixed explosives and the catalysis of burning. She considered sulphur in black powder to be a catalyst.

Here are the main conclusions of the work of Glazkova *et al.* [22] related to the burning of mixtures of inorganic nitrates with charcoal.

(1) Inorganic nitrates can play the part of catalysts and their effectiveness can be arranged in the following way:

$$Na > Pb > K > Ba > Al > Ca, Mg, Cu.$$

(2) A stoichiometric mixture of ammonium nitrate and charcoal reacts in the condensed phase and a similar mixture of sodium nitrate with charcoal in a gas phase (see above for the statement on burning a mixture of potassium nitrate).

(3) The burning rate of the mixtures depends mainly on the catalytic activity of cations and not on their concentration.

(4) The most effective catalytic action on the burning of mixtures with ammonium, potassium and sodium nitrate possess salts of Cr (VI), Cu(II), Pb (II) and sulphur. They are acting mainly on reactions in condensed phase, that is, with ammonium and potassium nitrate.

Explosive properties

A paper by Isaksson and Rittfeldt [23] described the examination of black powder of different origins. They came to the conclusion that samples of different origins can be identified on the basis of their combustion parameters.

Thus burning under atmospheric pressure can vary from 1.2 to 2.1 m/sec. In a closed vessel, the coefficient of vivacity $(dp/dt)_{max}$ can vary from 4000 to 10700 kg/sec.

The rate of burning of confined black powder can be as low as 170 m/sec for coarse powder [24] to 950 m/sec for fine powder [25]. For sulphurless powder the rate of burning is higher: 1500 m/sec according to Belyaev *et al.* [25].

Hygroscopicity of Black Powder

Potassium nitrate is non-hygroscopic, but black powder is relatively hygroscopic. Charcoal is responsible for the hygroscopicity of the mixture because of the high absorption power of charcoal. One of the methods of reducing the hygroscopicity is to mix charcoal with non-hygroscopic substances. This however may reduce the burning properties of the powder.

The method of mixing charcoal with sulphur (binary mixture) can be beneficial under the following conditions:

(1) all charcoal is mixed with sulphur,
(2) the temperature of mixing should be kept for a short time at approximately 120°C, that is, above the m.p. of sulphur,
(3) mixing is carried out in the air-tight container in an atmosphere of nitrogen, to prevent the oxidation of sulphur.

Manufacture of Black Powder

The classic method of manufacturing black powder comprises mixing the ingredients in a ball mill and finally in edge runners. The process has not changed in nearly a hundred years. However, recently an improvement has been introduced by Løvold [26] in the factory of Dyno industrier A.S., Nitedals Krudtvaerk, Nitedal in Norway. This method consists of mixing and milling all three ingredients in a single operation in a Jet-Mill (Fig. 88 [24]). The mill has no moving parts which is one of the safety factors. Compressed air is blown through a specially designed nozzle in the lower part of the mill and into the grinding chamber. The air leaves the nozzles with a very high velocity. The material to be crushed – a mixture of all three components as a continuous stream – is fed into the chamber where the collision of particles causes pulverization to the size distribution as follows [26]:

100% finer than 25 μm
95% finer than 15 μm
90% finer than 10 μm
83% finer than 5 μm

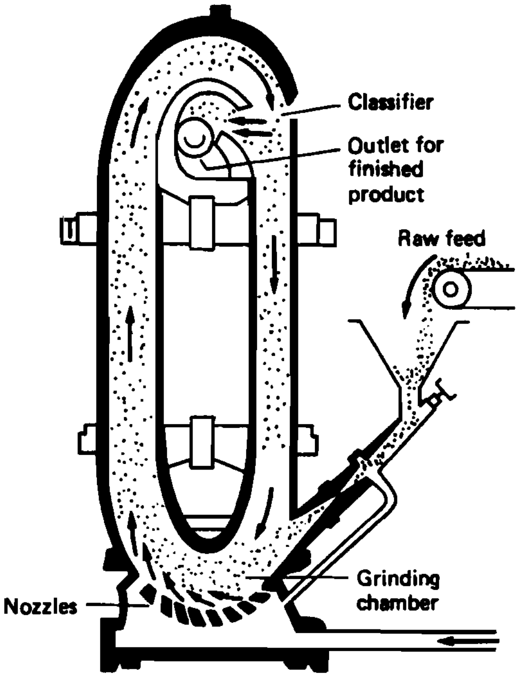


FIG. 88. Jet Mill of Nitedals Krudtvaerk, Norway for Compounding Black Powder according to Løvold [26] as given in S. Kaye, *Encyclopedia of Explosives*, Vol. 8, p. P517. ARRADCOM, 1978.

By changing the running conditions of the mill it is possible to get other particle sizes. The Jet-Mill is a central part of the new method of making black powder. However some old elements can be used. According to Løvold the process can be depicted by the scheme:

KNO_3+S+C → Weighing and Mixing Bin → Mixture bin (supplying continuously the required quantity of the mixture) → Jet-Mill → Cyclone → Press → Corning → Sieving → Polishing. The dust from the sieve goes back to the Cyclone.

Løvold has summarized the advantages of this new process as follows:

1. It is possible to operate the process automatically.
2. It is possible for one person to supervise the process by remote control.
3. The amount of explosive in the process is small.
4. The whole process can be carried out in one single room.

Although an explosion occurred at Nitedal in 1976, according to Biasutti [31] it was not connected with the manufacturing process. The explosion occurred outside the manufacture building.

The Use of Black Powder

1. Black powder with potassium nitrate and with sodium nitrate (the latter-German 'Sprengsalpeter') is widely used for mining when a low strength of explosive is required, for example in quarries where large and undamaged blocks are needed or when the material is soft (e.g. slate).
2. For slow burning fuses, delay charges.
3. For small rockets (signal, distress and life-saving at sea rockets), rockets for rain-making (Vol. III, p. 324).

Pyrotechnics

Pyrotechnics is strongly connected with black powder. This is however outside the scope of the present book. The existing literature is recommended [27–30].

Accidents with Black Powder

As mentioned earlier (Vol. III, p. 361) the manufacture of black powder is one of the most dangerous operations in the production of explosives. Before the advent of the manufacture of nitroglycerine it was considered to be the most dangerous type of manufacture. It still remains dangerous in spite of considerable improvement in the methods of production. In his book Biasutti [31] described an explosion in the edge runner at the factory in Modderfontein, South Africa in 1980. Nobody was injured thanks to the remote control operation.

History of Black Powder

The following are published monographs dealing specifically with the more recent history of black powder in various countries to complete the references in Vol. III, pp. 363–364: [32–36].

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CHAPTER 19

COMMERCIAL (MINING) EXPLOSIVES

(Vol. III, p. 395)

INTRODUCTION

The early history of the use of explosives in mines and in various branches of civil engineering has been described in Vol. III. The growing use of explosives for peaceful application has been described in a number of monographs. Here are some of them (in addition to those mentioned in Vol. III):

Assonov [1], Samujłło [2], Rossi and Pozdnyakov [3], Cybulski [4], Charewicz, Krawiec *et al.* [5], Dubnov, Bakharevich and Romanov [6], Fordham [7], *Mining Research*, Two Collective Vols (Ed. G. B. Clark) [8], the book on *Explosive Working of Metals* by Reinehart and Pearson [9].

According to the U.S. Statistics [10] the consumption of industrial explosives in the U.S.A. in 1979 and 1980 surpassed 4000 million pounds a year.

It should be added that in the U.S.A. commercial explosives can be classified as blasting agents and explosives [118]. The former are those which do not detonate from a detonator No. 8 but require a stronger initiator, while explosives detonate readily.

PRINCIPLES OF COMPOSITION OF COMMERCIAL EXPLOSIVES

The principles of the design of commercial explosives were described in Vol. III, pp. 420–440. Some of the principles will now be discussed in detail on the basis of more modern literature.

Oxygen Balance

The composition of commercial (mining) explosives should correspond to two requirements:

(a) production of non-toxic gases,
(b) full utilization of the energy of the reaction between the oxygen carrier and combustible ingredients.

The oxygen balance is usually calculated on the unwrapped explosive and, as Fordham [7] pointed out, only a part of the wrapper (waxed paper, polyethylene or other polymers) – usually a half – takes part in the chemical reaction. As pointed out in Vol. III (p. 424) both negative and positive balance can produce toxic gases: carbon monoxide and nitrogen oxides respectively. Dubnov *et al.* [6] pointed out that the explosive can also react with the medium surrounding the shot-hole.

Rossi [11] and Khudyakov [12] studied this problem and came to the conclusion that coal can react with CO_2 to yield CO, apatites and potassium salts can bind NO_2, molybdenum and some copper ores bind carbon monoxide. Some iron ores can catalyse the oxidation of carbon monoxide to carbon dioxide. Dubnov [6] pointed out that sulphur containing ore may be responsible for the formation of such toxic gases as SO_2 and H_2S.

Dubnov *et al.* gives the results of experiments in an apatite mine with Ammonit 6 as follows.

TABLE 76. Toxic gases produced by detonation of Ammonit 6 [6]

Combustible of the wrapper in g for 100 g of explosive		Oxygen balance %		Found in the atmosphere of the borehole l/kg	
Paper	Paraffin wax	Explosive	Cartridge	CO	NO_2
1.7	2.3	+0.3	– 9.8	30.1	3.4
1.7	4.8	+0.3	–18.3	34.1	3.4

Rossi, according to Dubnov reported that by replacing paraffin wax paper with polyethylene, the concentration of carbon monoxide was reduced from 39–42 to 12–20 l/kg, after the detonation of Ammonit No. 6.

Subsequently the official regulation in U.S.S.R. [13] reduced the amount of paper to 2 g and paraffin wax (or similar hydrophobic product) to 2.5 g/100 g of explosive.

Other factors influencing the formation of CO and nitrogen oxides:

The fineness of particles of ammonium nitrate reduces the amount of CO and NO, as given by Svetlov [11]: see Table 77.

Another factor influencing the composition of the products is the ratio between the diameter of shot-hole and the diameter of the cartridge. The following are data for Ammonit 6 Zh V [11]: see Table 78.

The composition of fumes produced by detonation of explosives used in Poland: Barbaryt A and Metanit D2 (Vol. III, pp. 478–479) was examined by Cybulska and Sobala [14]. The fumes were analysed after the detonation in both laboratory conditions and in shot-hole underground. Samples of gases

TABLE 77. Influence of the fineness of ammonium nitrate of the amount of toxic gases, according to Svetlov as reported by Rossi [11]

Explosive	Concentration of toxic gases, l/kg CO	NO
Ammonit No. 6		
large particles	28	9.8
fine particles	23.9	2
Ammonit PZhV-20		
large particles	23.8	5.8
fine particles	21.4	0.9

TABLE 78. Influence of the diameter of shothole and of the cartridges [11] explosive: Ammonit No. 6 ZhV

Diameters in mm		Concentration of toxic gases, l/kg	
Shothole	Cartridges	CO	NO
42	32	49–57	1.4–3.6
34	32	30–31	1.4–1.9

were taken 2 and 10 metres from the test site every three minutes for 30–40 minutes. The maximum concentrations were found as below:

CO	0.007–0.040%
NO_2	0.0055–0.010%

These concentrations decrease very quickly through the blowing ventilation. Overcharging of shot-holes produced a marked increase in the above gases. When fired in coal more fumes are produced than in stone.

Volk [15] examined the detonation fumes, between the detonation of Ammonit 1 in an atmosphere of air and argon. In the former case the amount of NO was higher than in argon, and the method of determining toxic gas products in the Federal Republic of Germany was described [16]. G. Persson and P. A. Persson [106] and Lindqvist and Johnson [107] found that experimental firing of charges of AN–FO explosives in steel-tubes gave results comparable with those in rocks. Similar results of firing charges in mortar were also reported [108].

HYGROSCOPICITY OF MINING EXPLOSIVES

The hygroscopicity of ammonium nitrate is a great drawback in explosives containing this salt. It limited the use of ammonium nitrate explosives, and only relatively recently methods were found of reducing the hygroscopicity of ammonium nitrate explosives.

One of the methods of protecting explosives against moisture consists in using a hydrophobic envelope, such as paper impregnated with hydrophobic substances more efficient than paraffin, such as paraffin with added substances containing polar groups – pitch, asphalt, petroleum tar etc. or using a polyethylene envelope.

A recent method of protecting ammonium nitrate against moisture, is mixing it with substances such as calcium or zinc stearate, petroleum tar, asphalt, barium sulphate and guar gum powder. According to Dubnov [6] stearates are in powder form of 5–20 μm size, whereas ammonium nitrate is of 70–120 μm. Owing to such sizes a very small proportion of stearates suffices to cover the surface of particles of ammonium nitrate. To evaluate the efficiency of the hydrophobic substances – Pozdnyakov in the U.S.S.R. [17] developed a hydrostatic apparatus which determines the pressure of water which is required to penetrate through a thin layer of explosive enclosed in a capsule. Dubnov [6] gives the figures for water pressure in centimetres needed to pass through a standard explosive composed of ammonium nitrate (80%), TNT (19%) and hydrophobic substance (1%). Some of his figures are collected in Table 79.

TABLE 79. Water column (in cm) needed to penetrate Poznyakov apparatus [6]

Calcium stearate	90 cm
Zinc stearate	88
Paraffin wax–petroleum tar (4:1)	85
Paraffin wax–asphalt (1:2)	82
Ferric stearate	78
Paraffin wax	70
Paraffin wax–calopheny (4:1)	68
Paraffin wax–soot (1:2)	67
Paraffin wax–graphite (1:2)	67
Paraffin wax–calopheny (3:1)	66
Paraffin wax–dinitronaphthalene (1:2)	64

Shestakov [18] introduced an original method of protecting ammonium nitrate which consists in mixing ammonium nitrate with $Fe_2(SO_4)_3$ (0.5%) and fatty acids (stearic, palmitic acid) (0.25%). A thin layer of ferric stearate or palmitate is formed on the surface of crystals of ammonium nitrate. It is now customary to use 0.3–0.4% fatty acids and 0.07% iron salts. Part of the fatty acids can be replaced by paraffins. Explosives containing fatty acids and iron salts are marked with symbol Zh V.

The mixing of ammonium nitrate with hydrophobic components is usually achieved in edge runners used extensively in black powder manufacture (Vol. III, p. 350, Figs 93, 94) or in disc mixers (Vol. III, p. 504, Fig. 166).

Water resistance of commercial explosives is examined in Germany at Test Station Dortmund – Derne [69].

A train of four cartridges is fixed in a file on a wooden board, the first of the cartridges is equipped with a detonator No. 8. Five longitudinal notches are cut into each cartridge. The train is immersed for 5 hours in 20 cm depth of water. After that they are detonated. The train must detonate entirely.

A similar test is used in the U.S.A. [69].

STABILITY OF COMMERCIAL EXPLOSIVES

Physical Changes

Ammonium nitrate commercial explosives are stable at a moderate temperature and dry atmosphere and should not be kept at temperatures above 32°C when a change in the crystal habit of ammonium nitrate occurs and the change of temperature may harden the cartridges. The same can occur if explosives are kept in a humid atmosphere and a change of temperature can produce cracking of ammonium nitrate.

Explosives with nitroglycerine should be protected from freezing and the thawing of frozen nitroglycerine can cause disasters (Vol. III, p. 518). Currently in most countries a non-freezing mixture of nitroglycerine with nitroglycol is used. The change of explosive properties on storage was discussed in Vol. III, pp. 436–438.

Chemical Changes

Ammonium nitrate is usually slightly acid owing to the loss of ammonia leading to the presence of free nitric acid. This can possess a deteriorating effect on nitrate esters present in the explosive. It is therefore advisable to include neutralizing agents, such as $CaCO_3$ and Centralites (Vol. III, p. 645). The latter in proportion of 0.5%. Diphenylamine can be used only in mixtures without aromatic nitro compounds, as diphenylamine reacts with higher nitrated aromatics. Ammonium nitrate explosives with nitrate esters and dynamites are usually subjected to the Abel-test at 80°C to verify their stability [19].

Apart from the reaction of the decomposition of nitrate esters some other changes can occur in mixed explosives, such as the reaction of the oxidation of aluminium, particularly marked in water–gel explosives. Also permitted (permissible) explosives containing ion exchange mixtures of sodium nitrate with ammonium chloride a double exchange reaction can occur:

$$NaNO_3 + NH_4Cl \rightleftharpoons NaCl + NH_4NO_3.$$

The reaction is reversible and ammonium nitrate can react with sodium chloride.

All the above considerations lead to imposing a limited storage time on mining explosives. In Poland ammonium nitrate permitted explosives should be used within 1½–3 months from the production date. Non-permitted ammonites and dynamites 2–4 months. In the U.S.S.R. ammonium nitrate explosives in cartridges should be used within 3 months.

RATE OF DETONATION AND CRITICAL DIAMETER

As is well known the rate of detonation of explosives depends on the density and diameter of cartridges. Figure 89 gives the rate of detonation against the diameter of cartridges of some mining explosives according to Cybulski [4].

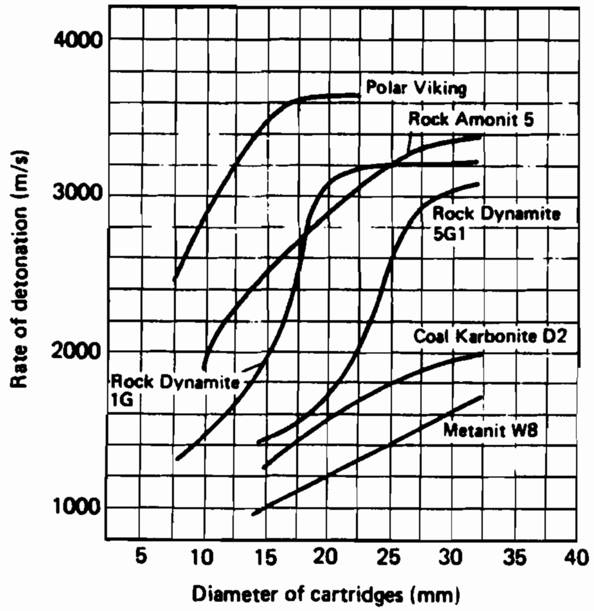

FIG. 89. Rate of detonation of typical mining explosives against diameter of cartridges [4].

Below a certain diameter detonation is not propagated. A definition of the critical diameter is as follows. The critical diameter is larger when the cartridges detonate in the open, and smaller when confined in metal tubes. Table 80 gives the figures according to Cybulski [4].

As is known, the rate of detonation depends on the confinement of the charges. Cybulski [4] gives some data collected in Table 81.

"GAP TEST" (TRANSMISSION OF DETONATION)

The gap test values depend, among different factors, on the density (see Vol. III, p. 436, Fig. 144), diameter (Table 82) and confinement (Table 83).

TABLE 80. Critical diameters of mining explosives according to Cybulski [4]

Explosives	Diameters in mm 100% detonation	 Possible detonation	 No detonation
Metanit powietrzny D2	20	15	10
Karbonit węglowy D2	25	15	13
Amonit skalny 5	10	–	8
Barbaryt powietrzny AG1	25	20	17
Dynamit skalny 1G1	12	8	6

TABLE 81. Dependence of the rate of detonation on confinement according to Cybulski [4]

Explosive	Diameter of cartridges mm	Density	Rate of detonation m/s In open	 In a shothole
Metanit powietrzny D2	36	0.71	1620	1920
Karbonit węglowy D4	36	0.71	1960	2330

TABLE 82. Dependence of the gap-test on diameter (Dubnov [6])

Diameter mm	Explosive AM 8 gap in cm	 AM 10 gap in cm
32	0–1	2–3
36	2–4	3–6
40	4–6	5–8
60	7–15	10–20
90	20–30	25–30

TABLE 83. Gap-test in open space and in a mortar. Initiation with detonator No. 8 according to T. Urbański [20]

Explosive	Density	Gap test, cm in open	 in mortar
Bradyt powietrzny C*	1.08	18	25
Bradyt powietrzny F**	1.06	15	24
A 2***	1.00	1.5	2.5
Miedziankit****	1.70	0	40

Compositions:

* 64.7% NH_4NO_3, 4% nitroglycerine, 8% TNT, 2% charcoal, 20% NaCl.

** Vol. III, p. 475.

*** 85.5% NH_4NO_3, 5.5% TNT, 9% nitronaphthalene and in addition ca. 1.5% mineral oil.

**** 90% $KClO_3$, 10% Kerosene (Vol. III, p. 278).

Gap Test and Temperature

The gap test depends on the temperature of explosives. Thus for a permitted explosive with 10% nitroglycerine–nitroglycol the gap was found to be 5 cm at −10°C, 6 cm at 0°C, 8 cm at 10°C and 10 cm at 20°C (see Dubnov *et al.* [6]).

A remarkable difference exists between the gap test in the open and in a mortar with the chlorate explosive Miedziankit. When initiated in open space with detonator No. 8 the detonation died away 7–10 cm beyond the detonator. On the contrary, in a mortar, no limit was found owing to the short borehole.

The problem of the cause of such a difference between ammonium nitrate and chlorate explosive has not been examined but certainly merits a special study.

Potassium chlorate is no longer used in explosives and is limited only to pyrotechnic compositions and match-head formulation [21]. Sodium chlorate is produced to manufacture chlorine dioxide as a bleaching agent of wood pulp and cellulose fibres.

The transmission distance of picric acid charges was examined by Burlot [22]. This is however outside the scope of the present book. Also the method of determining the transmission detonation through an inert solid medium, such as a number of card-boards ('card–gap test') [116, 117], cellulose acetate [121, 122] or Plexiglas layer is discussed in the literature on the theory of detonation, for example [34].

CHANNEL EFFECT

T. Urbański in 1926 [20] described the phenomenon currently known as channel effect (Vol. III, pp. 435–436). He found that several ammonium nitrate explosives in a steel tube produce a shock wave which moves at a velocity higher than the detonation wave. This is summarized in Table 84.

The author expressed the view that in a long bore-hole 'end' cartridges can be compressed to a high density ('dead pressed') which detonate with difficulty.

TABLE 84. Shock wave in open space and in a steel tube.
Initiation with detonator No. 8
according to T. Urbański [20, 33].
Explosive Bradyt F (see Table 83), cartridge 30 mm diameter

	In the open	In a steel-tube 35/42 mm
Detonation velocity m/s	2740	3220
Shock-wave m/s		
0–50 mm	1815	–
50–100 mm	560	3830

An unfavourable opinion of this work was given in [23]. The phenomenon was described in 1965 by Ahrens [24], Woodhead and Titman [25], and by Johansson and Persson [26]. Tribute was paid to the priority of the author of the present book by Golbinder, Svetlova and Tyshevich [27]. The latter authors contributed a considerable number of experimental facts on channel effect.

POSSIBLE SPIRAL WAY AND DETONATION OF MIXED EXPLOSIVES

Photographs of the detonation of ammonium nitrate explosives with an open lens camera were taken by T. Urbański [28]. The image was composed of light and dark bands with a sinusoidal shape. An hypothesis was advanced by the author of the possible spiral way of the detonation. At the same period British authors – Campbell, Bone *et al.* [29, 30] published a number of papers in which they indicated the spiral way of the propagation of detonation of gas mixtures. Their results were substantiated by Laffitte *et al.* [31].

T. Urbański continued his experiments with a camera giving images at 10^{-4} s intervals [32].

The conclusion was [33] that only mixed explosives, for example ammonium nitrate – TNT give the described pattern.

The latter fact was also observed by P. A. Persson and G. Persson [34] and they claimed that the pattern on the photographs was due to glass cracking. An argument against such a suggestion is that if a glass-tube is filled with an homogeneous explosive, for example TNT, Picric Acid or PETN, no sinusoidal pattern is observed, although the cracking is the same.

Another experiment by T. Urbański [33, 34] throws some light on the detonation of explosives, if the detonation was carried out in a plastic tube put concentrically inside another tube made of glass and *suspended* in air (Fig. 90). If the inner tube was filled with homogeneous explosive not a mixture, the inner tube remained undamaged after the detonation. If the inner tube is filled with a mixture (e.g. NH_4NO_3 and TNT) the inner tube was covered with holes (Fig. 91).

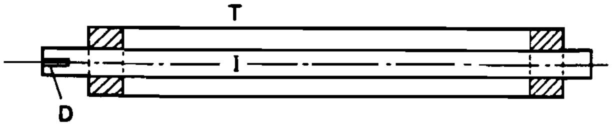

FIG. 90. Detonation in two concentric tubes: T – outer glass tube, I – inner celluloid tube filled with an explosive, D – detonator [32, 33].

The success of the experiment depends on the choice of the correct dimensions of the outer (glass) and inner (plastic) tube.

The fact that the inner tube filled with mixtures is perforated indicates that

FIG. 91. Inner celluloid tube after detonation of TNT/Ammonium nitrate 78/22 mixture, according to T. Urbański [32, 33].

the two solid phases forming an explosive mixture do not detonate simultaneously and this fact has some bearing on the pattern seen in the photograph.

It should also be recalled that the slow explosion of nitroglycerine can manifest a spiral mode of propagation [35].

DEFLAGRATION OF EXPLOSIVES IN COAL-MINES (Vol. III, p. 417)

The deflagration of explosives in coal mines was examined for the first time by Audibert and Delmas [36] and independently by Cybulski (Vol. III, p. 418) and showed that the decisive factor is the admixture of coal-dust to the explosive particularly in the vicinity of the detonator. Explosives containing nitroglycerine are more liable to deflagration and particularly chlorate explosives can create such a danger.

The problem of deflagration of ammonium nitrate explosives was extensively investigated by Andreev and co-workers [37]. Their conclusion was that the presence of wood meal increases the ability of such explosives to deflagrate and reduces the critical diameter of burning. Also the replacement of NH_4NO_3 + NaCl by $NaNO_3$ + NH_4Cl (Vol. III, p. 421) in mixtures containing TNT and nitroglycerine slightly increased the ability to deflagrate. Andreev and Glazkova [38] found that the ammonium nitrate/TNT mixture 80/20 burned faster under the action of the addition of potassium nitrate or potassium perchlorate. Further experiments by Glazkova and Zhadan [39] suggested replacement of ammonium chloride by ammonium oxalate.

According to Dubnov [6] the conditions of shot-firing which lead to a deflagration of mining explosives were recently established by Galadzhii and co-workers [40, 41], Dubnov and Romanov [42]. In principle deflagration can occur when the gap between cartridges is larger than that required to produce the detonation. Thus Dubnov and Romanov [42] describe three gap regions:

(a) transmitting the detonation,
(b) producing the deflagration,
(c) refusing any action.

This is depicted in Fig. 92 based on experiments [6].

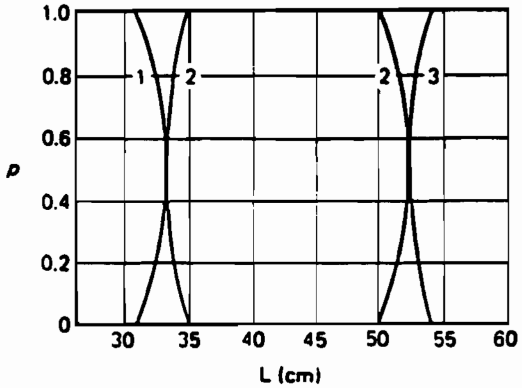

FIG. 92. Experimental curves of the probability p of detonation (1), burning (2) and no reaction (3) of a passive cartridge of cyclonite (dia. 35 mm, density $\rho = 1.2$) as a function of the distance L cm from the active cartridge of TNT (dia. 35 mm, $\rho = 1.0$) according to Dubnov *et al.* [6].

In the U.K. the ability of explosives to deflagrate is examined with the gap test by filling the gap with coal-dust.

The papers by Zimmermann [43] and Murray *et al.* [44] pointed out once more that the penetration of coal-dust into the explosive increases the danger of deflagration of the explosive. Further experiments on deflagration confirmed the influence of coal-dust on the ease of deflagration [102]. Some experiments were carried out to show the influence of deflagration on methane-air explosion [103].

EVALUATION OF THE STRENGTH OF MINING EXPLOSIVES

In addition to the laboratory methods which comprise mainly lead block expansion and the rate of detonation different methods of a more practical character are in use. Thus Cybulski [4] reported the method used in Poland which is essentially the method of bench firing and determining the burden which can be brought down by a charge of 200 g of explosive in a bore-hole of 80 cm length and stemming of 60 cm. This is presented in Fig. 93. In (a) the correct burden is shown and in (b) an overlarge burden is shown. The dimensions for a rock are referred to 200 g of Metanit D2 and stemming with lime.

Apart from such a practical method of determining the strength of explosives the following are the laboratory methods of examining the strength of explosives

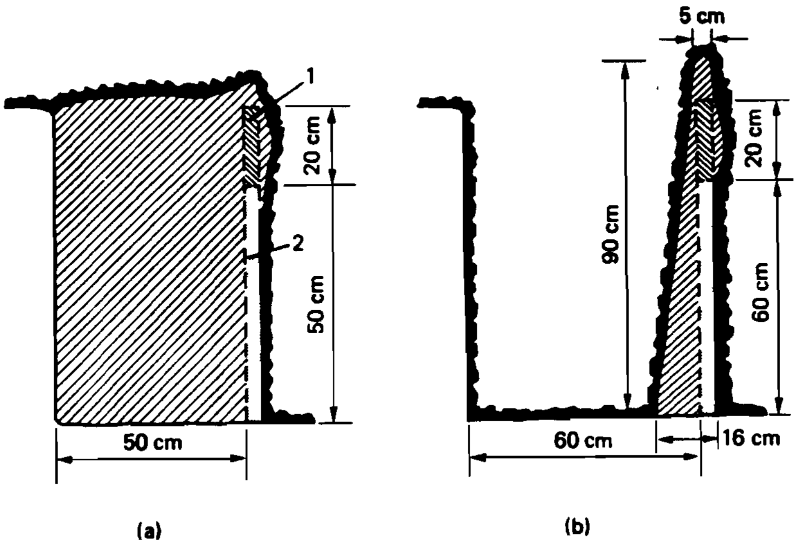

FIG. 93. Determination of the strength of an explosive by firing in a coal burden: (a) a correct burden (50 cm) (b) a burden too large (60 cm). Charge of 200 g Metanit powietrzny D2 (1), stemming (2), according to Cybulski [4].

(Fordham [7]): ballistic mortar, lead block expansion ('Trauzl block'), rate of detonation.

The International Study Group for the Standardization of the Methods of Testing Explosives, EXTEST has been in operation since 1960 (the original name was: The European Commission for the Standardization of the Methods of Testing Explosives). The early history of this organization has been presented by Ahrens [45]. The reader should consult this important paper which gives technical details for carrying out the testing of explosives, further developments have been reported by Persson [46].

Among the methods for determining the strength of explosives underwater detonation has been recommended. It was described for the first time by Sadwin, Cooley, Porter and Stresau [47]. The authors suggested that the method developed for testing military explosives [48] could be used for commercial explosives. Further examination of underwater detonation of explosives was described by Peterson and Begg [49], Fossé [50] and Bjarnholt [51]. All of these authors came to the conclusion that 'bubble energy' can be readily measured and forms the most useful criterion provided by the underwater test. It is not limited to gram quantities and can be used in charge dimensions comparable to those used in practical blasting, it is also simple and inexpensive. According to Fossé the charge is placed at a depth of 12.65 m in a basin 19 m deep and with a radius of 30 m. More recent experiments on underwater detonations have been reported [104]. Satyavratan and Vedam [105] found that a linear correlation exists between underwater energies and lead block expansion values.

SAFETY AGAINST METHANE AND COAL-DUST

This problem was fully discussed in Vol. III, pp. 409–491. A few more recent items of information will be given here.

The modern testing gallery in India is presented in Fig. 94.

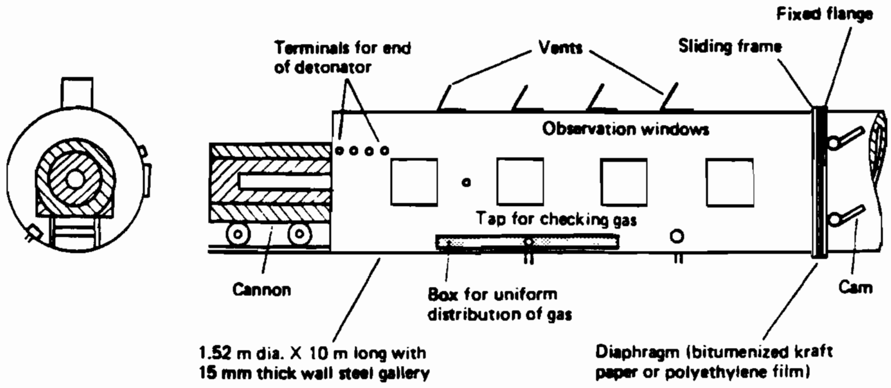

FIG. 94. Modern Cylindrical Steel Gallery for Testing Permitted Explosives (Courtesy IDL Chemical Ltd, Hyderabad, India).

As mentioned previously the result obtained in a gallery depends on the mode of initiation.

In the usual test the detonator is inserted last into the cannon, this is called direct initiation. If the detonator is placed at the opposite end of the train of cartridges and is inserted first into the cannon the initiation is called inverse and the probability of ignition of a methane–air mixture is very high. Figure 95, illustrates the difference between direct and inverse initiation according to Taylor and Gay [52].

More severe tests, known as 'Break Tests', exist in the U.K. a description of which was given in Vol. III, p. 419, Fig. 140. Here is the description according to Fordham ([7], pp. 79–82).

The tests were devised in the United Kingdom for studying the safety of explosives intended for use in ripping, i.e. increasing the height of roadways in mines after the coal has been extracted. The extraction of coal relieves stresses in the surrounding rocks and is therefore liable to cause breaks which can contain methane–air mixtures.

Break Test 1 consists of a shot-hole in which a break occurred across the hole in the middle of the explosive charge. It is simulated by placing a train of explosive across the gap between two steel plates in a test gallery.

Break Test 2 consists of a break parallel to the shot-hole in such a way that half of the shot-hole is in one piece of rock and the remainder of the explosive in the space between the rocks. It is simulated by two parallel plates of which the lower is grooved as a bore-hole – Fig. 96.

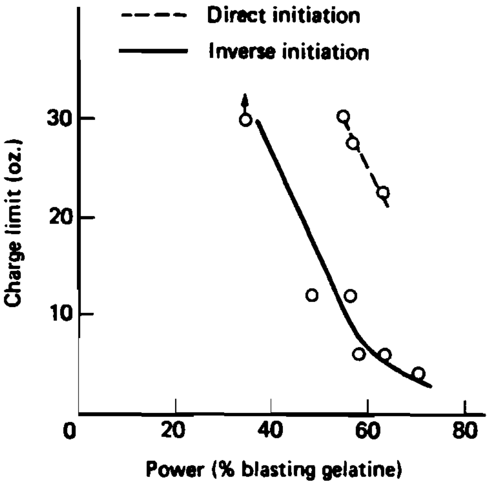

FIG. 95. Effect of initiation on gallery testing [7].

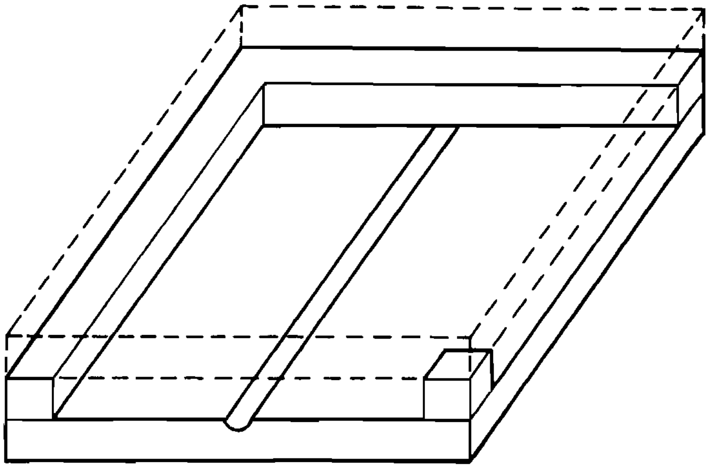

FIG. 96. No. 2 Break Test. The position of the upper plate is shown by the broken lines, according to Fordham [7].

Two heavy steel plates 1.8 m^2 are held 5 or 15 cm apart. The plates are in a gastight enclosure formed from steel sides with sheet polyethylene. The explosive cartridges are in the groove. The space inside the enclosure is filled with an explosive gas mixture. The ignition or non-ignition of the gas mixture is observed.

Break Test 3 consists of a break occurring at the end of a shot-hole. This is simulated by a cannon fired with the mouth in close proximity to a steel plate.

The most severe of these is Break Test No. 2.

In the U.S.S.R. a cannon spraying coal dust in quantity of 6 kg by means of a small (50 g) explosive charge. Coal dust of 400–600 g/m^3 is formed and the shot of the examined explosive is fired 2–10 s after spraying the dust.

The mechanism of the ignition of methane and coal-dust was summarized in diagram – Fig. 97 depicted by Cybulski [4].

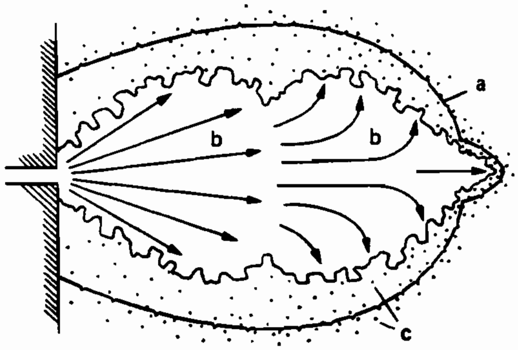

FIG. 97. Shock wave and products of detonation according to Cybulski [4]: (a) – shock wave, (b) gas products of detonation, (c) – solid particles of explosive.

Here three elements are shown of the projection from the mortar:

1. Shock wave,
2. Gas products of detonation,
3. Particles of the explosive mixture: undecomposed explosive, sodium chloride, metal parts of the detonator. Some of them are projected in front of the shock wave.

The necessity for standardization of gallery-tests as carried out in different countries has also arisen [109]. Gorol and Sobala [110] drew attention to their observation that the results against methane–air was a better practical criterion of the safety of explosives than the test against coal-dust.

Theory of Safety Against Methane and Coal-Dust

The theoretical aspect of inhibition of explosions of methane–air and coal dust–air is mainly regarded from the view point of the action of alkali metals in flame and particularly on the action of potassium ion [53–55].

Ashton and Hayhurst [56] rationalized it in terms of collisional ionization and recombination of electrons with alkali metal ions in flame, for example:

$$M + X \longrightarrow M^+ + e^- + X.$$

Where X is a flame species.

AMMONIUM NITRATE–FUEL OIL MIXTURES (AN–FO)

(Vol. III, pp. 482, 508)

As described in Vol. III, p. 482 the cheapest ammonium nitrate explosives (AN–FO) were introduced in opencast mines. Diesel fuel-oil was used as a cheap combustible ingredient – originally in 1954 and eventually on a larger scale in 1960 in the U.S.A. [57, 72] and almost simultaneously in Canada, Scandinavia and Germany [58], Japan and in U.S.S.R. [59].

The following are figures on the use of AN–FO explosives in the U.S.A. in 1979 and 1980: over 1300 and nearly 1400 million pounds respectively. Their use was mainly in quarrying, non-metal mining and construction work [10].

An International Symposium on Mining Research took place in 1961 [60] and was partly dedicated to AN–FO explosives. Hino and Yokogawa [61] described the action of surfactants on the detonation ability of ammonium nitrate and its mixtures with coal tar in proportions 93.3/6.2. The addition of 0.5% of surfactant increased the detonation ability of the mixtures. Particularly effective were sodium dinaphthylmethane disulphonate, sodium laurylsulphonate and sodium dodecylbenzene sulphonate.

Grubb [62] drew attention to the importance of the intimacy of mixing ammonium nitrate with fuel oil by using fine and porous particles of ammonium nitrate and Clark *et al.* [63] described the use of micro-prilled ammonium nitrate of less than 20 mesh size. They found the AN–FO made of such ammonium nitrate can readily detonate but the rate of detonation is limited by characteristic low bulk density – the consequence of micro-prills.

The possible use of AN–FO explosives for underground work was described by Henning [64] and Bullock *et al.* [65]. The authors came to the conclusion that AN–FO can replace dynamite in blasting operations even in small diameter holes (e.g. 23 mm [64]). An important problem for underground work is fumes produced by AN–FO. This was investigated by Van Dolah *et al.* [66]. Their main conclusions are in agreement with general rules: the negative oxygen balance favours the formation of CO but does not reduce the amount of NO_2. The positive balance appreciably increases the concentration of NO_2. The strength of the primer also has an influence on the composition of the products. The concentration of oxides of nitrogen increased as the strength of the primer decreased.

According to Schiele [58] the maximum rate of detonation is with 5.5% diesel oil. Chaiken, E. B. Cook and Ruhe [114] used the large closed gallery to examine both the rate of detonation of AN–FO and the composition of gaseous products. Figure 98 gives the rates of detonation of AN–FO made of prilled and powdered ammonium nitrate. Ammonium nitrate was catalysed by 4% of undisclosed catalyst. The formation of nitrogen oxides was favoured by inadequate initiation and propagation of detonation, as already known [115]. The rate of detonation against the diameter of cartridges is changing as depicted in Fig. 99.

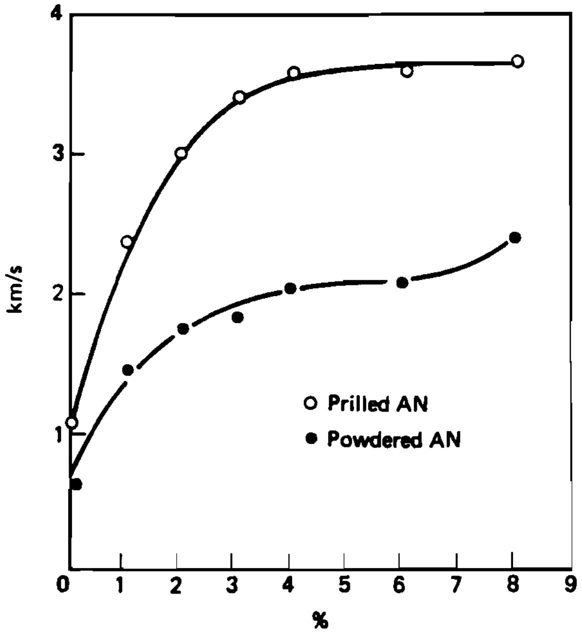

FIG. 98. Rate of detonation of AN–FO (with prilled and powdered AN) as a function of the proportion of Diesel oil diameter 14 cm [114].

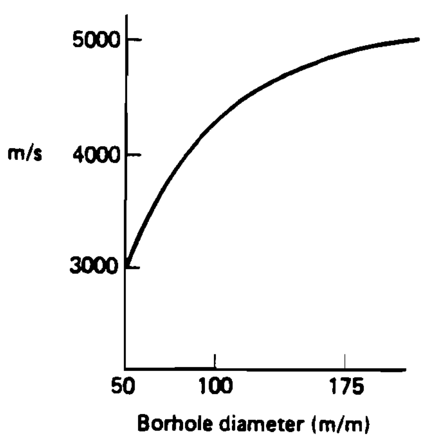

FIG. 99. Rate of detonation of AN–FO as a function of bore-hole diameter (Schiele [58]).

EXPLOSIVE WORKING OF METALS

A low rate of detonation is required for most operations connected with explosive working of metals. It is usually achieved by mixing explosives marked for their ease of detonation (such as PETN, Cyclonite) with a relatively large quantity of such oxygen carriers as $NaNO_3$, KNO_3, $Ba(NO_3)_2$.

Plastic explosives are particularly suitable for the working of metals.

Most problems connected with explosive working of metals are outside the scope of the present book and the monograph [120] should be consulted.

MINING EXPLOSIVES USED IN VARIOUS COUNTRIES

Below are listed mining explosives used in some countries which complete the list given in Vol. III, pp. 446–489. In addition to the list a separate group is described:

Water gel (Slurries), p. 545.

Bulgaria

Bulgarian Permitted Explosives are characterized by the presence of potassium sulphate as the agent giving safety to methane and coal-dust [68]: Table 85.

TABLE 85. Bulgarian permitted explosives

Components	Skalinit 1	Skalinit 2
NH_4NO_3	69	64
$K NO_3$	–	5
TNT	15	15
Charcoal	1	1
K_2SO_4	15	15
Oxygen balance %	+1.37	+2.63
Heat of detonation (calculated) Kcal/kg	720	685
Calculated temperature of explosion °C	2295	2295
Rate of detonation m/s	3435	3200
Lead block cm^3	300	280
Gap test cm	4	3

Germany (Vol. III, p. 455)

German Permitted Explosives are, as before, divided into three classes. Their composition still remains undisclosed and the method of manufacture is kept secret.

Two main groups of Permitted Explosives are known: those made by Vasag-chemie Synthen GmbH: Wetter-Devonit A, Wetter-Roburit B, Wetter-Salit A, Wetter-Securit C, Wetter-Wasagit B, Wetter-Westphalit B, and made by Dynamit Nobel A.G.: Wetter-Carbonit C, Wetter-Energit B, Wetter-Nobelit B.

Their properties are collected in Meyer Dictionary [69].

Great Britain (Vol. III, p. 461)

Permitted explosives. The five groups of permitted explosives used in the U.K. are now called P explosives with numbers P1 to P5.

P1 Explosives should pass the following test [7]

(a) 26 shots fired of 142 g of explosive with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture
(b) 5 shots fired of 795 g with direct initiation, stemmed, should not ignite methane–air mixture
(c) 5 shots fired of 795 g with direct initiation stemmed, should not ignite coal dust–air mixture.

Their power should not be larger than 58–66% of blasting gelatine [7]. Polar Ajax and Polar Viking are typical representatives of this group of explosives (Vol. III, pp. 466 and 468 respectively).

One more explosive P1 should be mentioned: Hydrobel of the composition given in Table 86.

TABLE 86. British permitted explosives

Components		Explosives	
	Hydrobel (PI)	Unipruf (P3)	Carrifrax (P4)
NH_4NO_3	20	53	10
$NaNO_3$	–	–	46.5
Liquid nitrate esters	40	8	9
Nitrocellulose	2	–	–
NaCl	27	29	–
NH_4	–	–	28
$BaSO_4$	9.5	–	–
Combustible (e.g. wood meal)	1	9.5	6
Others (e.g. hydrophobic compounds)	0.5	0.5	0.5

P2 Explosives are sheathed explosives (Vol. III, p. 431).

They have been almost entirely withdrawn owing to the danger of breakage of the sheath and therefore loss of safety. According to Fordham [7] they have been superseded by P3 explosives.

P3 Explosives are so called Eg.S. explosives – Vol. III, p. 429. Currently these explosives should pass the following [7] test:

(a) 26 shots fired of 397 g with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture.
(b) 5 shots fired of 1020 g with direct initiation stemmed should not give ignition of methane–air mixture.
(c) 5 shots fired of 567 g with inverse initiation unstemmed should not give an ignition of coal dust–air mixture.

Their power should not be higher than 42–50% of blasting gelatine. Unigel and Unigex are typical representatives of this group of explosives (Vol. III, p. 466).

One more explosive P3 should be mentioned: Unipruf (Table 86).

P4 Explosives were designed for ripping with delay detonators. They should satisfy the following tests [7]:

(a) as with P3 explosives,
(b) 5 shots fired of the maximum permitted charge weight in Break Test I should not give an ignition of methane–air mixture.
(c) 26 shots are fired in Break Test II in a gas mixture of 3.6% propane with air and nitrogen which is more easily ignited than methane–air. Preliminary shots determine the most hazardous charge of explosive not exceeding 227 g. No more than 13 ignitions may occur.
(d) 5 shots of a cartridge of 30.5 cm long and 3.7 cm diameter are fired in Break Test III and no ignition should occur.

Carrifrax is the typical explosive P4 (Table 86).

P5 Explosives are designed for blasting solid coal with millisecond delay.

26 shots of 567 g are fired into methane–air mixture and no ignition should occur. In addition the explosives should pass the second (b) and third (c) test applied to P3 explosives.

Italy

Italian mining explosives are described in the Encyclopedia by Fedoroff, Sheffield and Kaye [70].

Four groups of explosives are listed.

(1) *Mining explosives with nitroglycerine*. These contain 43–77.5% nitroglycerine with collodion cotton (1.5–5.0%) and oxygen carriers: NH_4NO_3, $NaNO_3$ or KNO_3. An exception exists with 7.0% nitroglycerine, 0.8% collodion cotton, 44% ammonium perchlorate, 32.2% sodium nitrate, 10% DNT, 5% TNT, 1% wood meal.

Another group consists of gelatinous explosives with 82.5–92% nitroglycerine and 5.5–8% collodion cotton. The former contains sodium nitrate (8.5%) and wood meal (3%).

(2) *Mining explosives with 4–14% nitroglycerine, and 0.1–1.5% collodion cotton.* A characteristic feature is the presence of a large quantity of ammonium picrate: 51–89% and one of the mixtures has 65% cyclonite.

(3) *Mining explosives without nitroglycerine with ammonium nitrate and TNT.* The aromatic nitro compounds are sometimes replaced with 10–30% PETN or Cyclonite. The names are: Ager, Vulcania, Vulcanite.

(4) *Mining explosives with ground smokeless powder.* These are mainly ballistite mixed with oxygen carriers, mainly ammonium nitrate.

Novel Mining Explosives used in Poland

As previously described (Vol. III, p. 475), mining explosives in Poland are divided into four groups:

I. Rock explosives (wrapped in red paper) (Tables 85–87)
II. Coal Explosives (Karbonits) (wrapped in blue paper)
III. Permitted explosives (Barbarits, Metanits) (in yellowish paper)
IV Permitted special explosives (Special Metanits) (in yellowish paper with two black bands) (Tables 87–91).

TABLE 87. AN–FO type Polish explosives

Ingredients	Saletrol A	Amonit Skalny I H
NH_4NO_3 (prilled)	94.5	90
Lubricating oil	5.5	–
Petroleum tar	–	2
Wood meal	–	8
Oxygen balance %O	0.0	+0.06
Lead block expansion cm^3	205	235
Rate of detonation m/s	3560	2630

According to their composition they are marked with letters:

G – denotes the presence of glycol dinitrate ('nitroglycol'),

J – means that they are ion exchanging mixtures (Vol. III, p. 421) containing $Na^+NO_3^- + NH_4^+Cl^- \longrightarrow Na^+Cl^- + NH_4^+\ NO_3^-$,

H – denotes hydrophobic properties of the ingredients, particularly that ammonium nitrate contains hydrophobic compounds, such as calcium stearate.

Most of the explosives described overleaf were introduced between 1975 and 1978.

TABLE 88. Polish rock explosives (Amonits)

Ingredients	Explosives: Amonit Skalny					
	6 G	11	11 G	12 GH	14 GH	15 GH
NH_4NO_3	81	85	85	81.4	86.5	82
Nitroglycerine	2	5.5	2.75	3.5	2.25	2.88
Nitroglycol	2	–	2.75	3.5	2.25	2.87
DNT	–	1.5	1.5	–	–	–
TNT	8	–	–	4	–	–
Petroleum tar	–	–	–	–	1.8	1.25
Wood meal	2	7.5	7.5	2	7.2	4
Al	5	–	–	5	–	7
Ca Stearate	–	0.15*	–	0.5	–	–
Lubricating oil	–	0.5	0.5	–	–	–
Fe_2O_3	–	–	–	0.1	–	–
Oxygen balance %0	+3.35	+3.97	+3.61	+4.92	+2.0	+0.85
Lead block expansion cm^3	420	330	310	370	315	400
Rate of detonation m/s	3030	2480	2000	3000	2600	2800
Gap test cm	13	9	5	14	4	8

* Over 100%

TABLE 89. Polish rock explosives (Dynamites)

Ingredients	Dynamit Skalny			
	3 GH2	5 G1	5 G3	8 GH
NH_4NO_3	47.9	50	50	47.4
$NaNO_3$	–	14.8	15.5	–
Nitroglycerine	22.5	11	11.5	22.5
Nitroglycol	22.5	11	11.5	22.5
DNT	2	4	10	2
TNT	–	7	–	–
Collodion cotton	2	0.8	1.0	2
Wood meal	3	1	0.5	3
Ca Stearate	–	–	–	0.5
Glycol	–	0.3	–	–
Fe_2O_3	0.1	0.1	–	0.1
Oxygen balance %0	+3.5	+5.87	+5.3	+2.02
Lead block expansion cm^3	430	320	320	420
Rate of detonation m/s	2370	2120	2800	2200
Gap test cm	7	6	8	11

TABLE 90. Polish coal and permitted explosives (Karbonits and Metanits respectively)

Ingredients	Karbonit weglowy D6G	Metanit powietrzny		Metanit powietrzny specjalny J1
		D5G	W2A	
NH_4NO_3	77	63.5	56	–
$NaNO_3$	–	–	–	53.8
Nitroglycerine	4	2	2.5	7.8
Nitroglycol		2	2.5	2.2
DNT	5	3.5	3	–
Wood meal	3.5	3	4	2.2
NaCl	10.5	26	25	–
NH_4Cl	–	–	7	34
Soot	0.1*	–	–	–
Dyestuff	–	–	0.1	–
Oxygen balance %0	+5.3	+4.96	+0.4	+7.55
Lead block expansion cm^3	265	200	180	100
Rate of detonation m/s	2150	2035	1900	1700
Gap test cm	7	4–6	3	5

* Over 100%

TABLE 91. Polish permitted explosives (Dynamite type)

Ingredients	FGH	Barbarit FGH 2	KG
NH_4NO_3	14.2	12.2	15
$NaNO_3$	–	–	15
Nitroglycerine	26.5	28	11
Nitroglycol	7.5	5	11
Centralit II	0.5	0.5	–
Collodion cotton	1	1	0.4
NaCl	40	43	34.5
NH_4Cl	–	–	10
$BaSO_4$	10	10	0.5
$CaCO_3$	0.3	0.3	–
H_2O	–	–	0.6
Oxygen balance %0	+2.15	+1.8	+3.56
Lead block cm^3	175	160	150
Rate of detonation m/s	2250	2000	2150
Gap test cm	12	4–5	4–5

Spain

According to Fedoroff and Sheffield [71] original types of explosives were developed during World War II by Ottaolauruchi: Esplosivo F.E.1, F.E.2 and F.E.3.

They were composed of 65–70% NH_4NO_3, 17–25% TNT and 10–15% $Na_2HPO_4 \cdot 7H_2O$.

Sweden

A few AN–FO Type explosives used in Sweden are given in Table 92 [67].

TABLE 92. AN–FO explosives used in Sweden [67]

Components	AN–FO–0	AF–FO–2	AN–FO–4	AN–FO–8
NH_4NO_3	94.5	92.9	91.4	88.2
Fuel Oil	5.5	5.1	4.6	3.8
Al	–	2.0	4.0	8.0

U.S.S.R. Mining Explosives [6]

Mining explosives in U.S.S.R. are divided into six groups.

I. For open cast work: Akvatols, Igdanit (AN–FO), TNT, TNT + Al (Table 93).
II. For open-cast and underground work, where no dangerous coal-dust and methane are present (Tables 94, 95).
III. Permitted explosives safe to methane but not for coal mines. (Table 96).
IV. Permitted explosives safe to methane and coal-dust (Table 96).
V. High safety permitted explosives (Table 97).
VI. Highest safety permitted explosives in particularly dangerous coal mines (Table 97).

Ammonits and ammonals. These are used in cartridges of 32 and 90 mm diameter. Most popular is Ammonit 6Zh V with ammonium nitrate protected by fatty acids and iron salts.

Some of the most popular compositions are given in Table 94.

The density of the explosives is comprised between 0.95 and 1.15 Ammonit Skalnyi No. 1 is also manufactured in compressed cartridges of density 1.43–1.53.

A modification of Ammonits are Zernogranulits. They contain ammonium nitrate in prills mixed with molten TNT. Those with a negative oxygen balance are used obviously in open-cast work only. Thanks to a high TNT content they are relatively hydrophobic. Some of Zernogranulits are described in Table 95.

TABLE 93. AN–FO type explosives used in U.S.S.R. [6]

	Dynamon AM–10	AC–8	Granulit AC–4	C–2	Igdanit
NH_4NO_3	87.7	89	91.8	92.8	94.5
Mineral Oil	2.3	–	–	–	–
Diesel Oil	–	3	4.2	4.2	5.5
Al	10	8	4	–	–
Wood meal	–	–	–	3	–
Oxygen balance % O	+0.25	+0.34	+0.41	+0.06	+0.14
Heat of detonation kcal/kg	1295	1240	1080	915	920
Volume of gases l/kg	800	845	910	985	980
Lead block cm^3	425–460	410–430	390–410	320–330	320–330
Rate of detonation m/s = 1–1.3 40 mm dia. in steel 10 g booster	4100–4300	3000–3600	2600–3200	2400–3200	2200–2800
Gap test cm					
dia. 32 mm	2–3				
40	5–8				
90	25–30				
100	–	0–4	0–2	–	–
Moisture % H_2O					
in open pit		5	3	5	
underground		2–3	1–2	2–3	

Dynamon AM–8 differs from Dynamon AM–10 by a lower aluminium and higher mineral oil content: 8% and 3% respectively.

The density is comprised between 0.80 and 0.95.

Permitted explosives are described in Tables 96 and 97.

Detonits and dynamites. Detonits are rock explosives used in the U.S.S.R. which contain 6–15% nitroglycerine and nitroglycol. Particularly popular is Detonit M of the composition:

NH_4NO_3 mark ZhV 78%
(hydrophobic)
Low freezing nitrate esters 10%
Collodion cotton 0.3%
Al 10.7% and
Ca or Zn stearate in addition (over 100%) – 1%.

Oxygen balance is +0.18%, lead block expansion 460–500 cm^2, rate of detonation in cartridges of

TABLE 94. Ammonium nitrate explosives in U.S.S.R. [6]

Components	Ammonits		Ammonal	Ammonit	Skalnyi
	No. 6 ZhV	No. 10 ZhV	VA–4	Skalnyi (rock) No. 1	(rock) Ammonal No. 3
NH_4NO_3 (hydrophobic)	79	85	80.5	66	72
TNT	21	8	15	5	5
Wood meal	–	7	–	–	–
Al	–	–	4.5	5	8
Cyclonite	–	–	–	24	15
Oxygen balance %0	–0.42%	+1.53%	+0.18	–0.79	–0.78
Lead block expansion cm^3	360–380	300–320	410–430	450–480	450–470
Rate of detonation m/s	3600–4800	3200–3600	4000–4500	4800–5300	4000–4500
Critical diameter in open m/m	10–13	15–20	12–14	5–6	8–10
Gap test cm for diameter 32 mm	3–6	2–5	5–8	10–14	8–12

TABLE 95. Zernogranulits and Grammonals in U.S.S.R. [6]

Components	Zernogranulits				Grammonals	
	79/21	30/70	50/50–V	30/70–V	A–8	A–45
NH_4NO_3	79	30	50	30	80	40
TNT	21	70	50	70	12	45
Al	–	–	–	–	8	15
Oxygen balance %0	+0.02	–0.45	–27.15	–45.9	–0.24	–38.65
Lead block expansion cm^3	360–370	330–340	340–350	330–340	420–440	440–460
Rate of detonation m/s	3000–3600		3600–4200	3800–4500	3800–4000	5800–6300
Critical diameter in open mm	50–60	40–60	40–50	40–60	30–40	60–80

TABLE 96. Permitted explosives in U.S.S.R. [6] Class III and IV

Components	Class III Ammonit AP–4ZhV	 Ammonit AP–5ZhV	 Pobedit VP–4	Class IV Ammonit PZhV–20	 T–19
Ammonium nitrate ZhV	68	70	65.5	64	61
TNT	17	18	12	16	19
Nitrate esters	–	–	9	–	–
Wood meal	–	–	1.5	–	–
NaCl or (KCl)	15	12	12	20	20
Oxygen balance %0	+0.45	+0.16	+0.48	+0.4	–2.47
Lead block expansion cm^3	285–300	320–330	320–340	265–280	270–280
Rate of detonation m/s	3600–4200	3600–4600	3800–4600	3500–4000	3600–4300
Gap test:					
cm diameter	5–10	5–10	6–25	5–10	5–10
36 mm diameter after 1 hr in water	4–6	4–7	5–20	4–7	2–4

Density: 1.0–1.2.

They do not ignite methane when 600 g fired with stemming of 1 cm.

Class IV: in addition they do not ignite coal dust when 700 g fired without stemming.

TABLE 97. Permitted, Class V and VI [6]

Components	Uglenit E–6	Class V Selectit granulated	Uglenit No. 5	Class VI Uglenit No. 7
NH_4NO_3 Zh V		66.5	14	–
$NaNO_3$ or (KNO_3)	46.3	–	–	(57)
Nitrate esters	14.2	10	10	10
Wood meal	2.5	8.5	1	2
NaCl or (KCl)	(7)	15	75	–
NH_4Cl	29	–	–	30
Stearates	1	–	–	–
Diatomite or PCV	–	–	–	1
Oxygen balance %0	+0.53	–0.2	+0.13	+4.94
Lead block expansion cm^3	130–170	220–240	60–90	100–120
Rate of detonation m/s	1900–2200	1800–2000	1750–1900	1600–1800
Gap test– cm diameter 36 mm	5–10	5–7	3–10	3–10

They do not ignite methane when the cartridge of 200 g of Uglenit E 6 or Selectit is suspended in experimental gallery.

The same with cartridges of: Uglenit No. 5 (500 g) and Uglenit No. 7 (1000).

24 mm diameter 3900–4300 m/s
32 mm diameter 4800–5000 m/s.
Critical diameter (in open) 8–10 mm
Gap test: 24 mm diameter 6–12 cm and
32 mm diameter 16–22 cm.

After keeping under water the figures are 4–8 cm and 10–15 cm respectively.

Density 1.1–1.3.

Dynamites which contain a higher proportion of nitrate esters, for example 62% are very little used in U.S.S.R. and form only 0.2–0.3% of the total production of explosives. The main objection is low shelf life and misfiring which have produced a number of accidents.

Permitted in Sulphur Mines and Oil Fields

In sulphur mines Sulphur Ammonit No. 1 ZhV and in oil fields Neftyanoi Ammonit No. 3 are used. Their properties were given in Vol. III, pp. 488–489 and the composition is given below (Table 98).

TABLE 98 [6]

Components	Sulphur Ammonit No. 1 ZhV	Neftyanoi Ammonit No. 3
NH_4NO_3, ZhV	52	52.5
TNT	11.5	7
Nitrate esters	5	9
Wood meal	1.5	–
KCl	–	30
NH_4Cl	30	–
Stearates	–	1.5
Oxygen balance %0	−1.0	−0.7
Lead block expansion cm^3	200–220	220–240
Rate of detonation m/s	2500–3000	2800–3200
Gap test: cm	5–10	3–7
after storage in water for 1 hour	3–7	2–5
Ignition test in an experimental gallery	400 g in a mortar does not ignite sulphur dust suspension	400 g in a mortar does not ignite methane with petroleum vapour

Modern Japanese Mining Explosives [*] (Vol. III, p. 468).

Recent information about some Japanese mining explosives are given in Tables 99–104.

TABLE 99. Rock explosives

Ingredients	Explosives Sakura dynamite	Tokugiri dynamite	No. 3 Kiri dynamite	No. 2 Enoki dynamite	Akatsuki† dynamite
Nitroglycerine/nitroglycol mixture 60/40 gelatinized with nitrocellulose	48–55	35–54	18–24	20–27	5–20
Nitro Compounds (DNT, DNX, TNT)	–	–	0–9	2–9	0–10
NH_4NO_3 and sodium and potassium nitrate	34–42	39–60	65–75	50–72	60–85
Sawdust	8–12	2–8	1–11	4–8	1–5
Properties					
Density	1.45–1.55	1.40–1.50	1.30–1.45	1.30–1.45	1.25–1.45
Lead block cm^3	320–360	430–480	380–430	270–430	370–430
Detonation velocity m/s	5500–6100	6500–7200	5500–6500	5800–6500	5000–5500
Gap test (as the multiple of charge diameter)	5–7	6–8	4–6	4–6	2–6

† For open-pit work.

[*] According to: Kogyo Kayaku Handbook, The Industrial Explosives Society of Japan, Tokyo, 1977, Makoto Kimura, Sumitomo Corporation in Tokyo, and K. Yamamoto of Nippon Kayaku Co. Ltd.

TABLE 100. Japanese permitted explosives containing nitrate esters (more than 7%)

Ingredients	Explosives No. 1 Toku-Ume dynamite	No. 3 Shiza-Ume dynamite	No. 3 Toku-Shiraume dynamite	EqS Bakuyaku
Nitrate esters (as in Table 99)	18–23	18.7	18–20	9–12
Nitro Compounds (as in Table 99)	4–8	3.0	–	–
Inorganic nitrates (ammonium, sodium potassium)	50–55	49.5	50–46	50–55
Sawdust	1–3	3.8	2–4	5–10
Sodium chloride	20–26	25.0	25–27	30–34
Properties				
Density	1.35	1.40	1.35–1.45	0.95–1.05
Lead block cm^3	290–310	280–300	300–320	170–230
Detonation velocity m/s	5500–6000	5500–6000	5500–5800	2700–3300
Gap test (as in Table 99)	5–7	5–7	5–7	3–6

TABLE 101. Japanese permitted explosives containing less than 7% of or no nitrate esters

			Explosives		
Ingredients	No. 5 Shouan-Bakuyaku	G Shouan-Bakuyaku	No. 105 Shouan-Bakuyaku	No. 2 Kurotaka Shouan-Bakuyaku	EqS-1 Bakuyaku
Nitrate esters (as in Table 99)	–	6.2	5–6	–	–
Nitro Compounds (as in Table 99)	5–8	–	–	4–6	5–7
Inorganic nitrates (as in Table 99)	75–80	69.8	67–73	76–80	63–71
Sawdust	4–6	9.0	6–11	4–7	10–14
Sodium chloride	11–13	15.0	14–16	4–7	25–30
Properties					
Density	1.0	1.0	0.95–1.05	1.0	1.0
Lead block cm^3	270–290	280–300	280–300	270–290	205–215
Detonation velocity m/s	4500–5000	3300–3800	3400–3600	4500–5000	3000–3500
Gap test (Table 99)	2–4	3–5	3–5	>2	>2

TABLE 102. Japanese perchlorate explosives (Vol. III, p. 474, Table 136)

		Carlit Explosives	
Ingredients	No. 5 Kuro Carlit	Akatsuki Carlit	Ao Carlit
Ammonium perchlorate	73–78	22–27	17–22
Nitro Compounds	–	2–7	2–7
Inorganic Nitrates	–	60–70	60–70
Sawdust	6–11	8–13	8–13
Ferro-Silicon	13–18	2–7	2–7
Properties			
Density	1.10–1.15	1.10–1.15	1.05–1.10
Lead block cm^3	440–470	390–440	380–440
Detonation velocity m/s	4000–4500	4000–4500	3700–4200
Gap test (Table 99)	4–6	3–5	3–5

TABLE 103. Miscellaneous Japanese commercial explosives

Ingredients	Urbanite	Explosives Dai Happa yo Bakuyaku	Akatsuki Bakuyaku
Nitrate esters	50–54	5–7	–
Nitro compounds	2–6	10–15	6–8
Inorganic nitrates	36–44	75–78	81–84
Sawdust	2–6	3–6	6–8
Al	–	–	2–4
Properties			
Density	1.30–1.40	0.98	1.0
Lead block cm^3	420–470	380–400	380–400
Detonation velocity m/s	2000–2500	3800–4300	4400–4600
Gap test (Table 99)	6–8	–	2–3
Used in	Urban blasting	Large blasting	Open pit

TABLE 104. Japanese 'TNT commercial' explosives

Ingredients	Explosives No. 2 Kohzumite	No. 12 Kohzumite	No. 31A Kohzumite*
TNT	15–30	6–15	100
RDX	0–10	11–20	–
Inorganic Nitrates	50–80	43–85	–
Ammonium perchlorate	0–8	–	–
Al	0–5	0–6	–
Sawdust	0–15	1–3	–
Properties			
Density	1.10	1.03	1.12
Lead block cm^3	450–480	380–400	310–350
Detonation velocity m/s	5300–5500	4800–5000	5500–5600
Gap test (Table 99)	5–6	4–5	

* For open pit work.

Belgium

The composition of typical permitted explosives made in Belgium are given overleaf (Table 105), according to Goffart and Waterlot [119]. The explosives belong to ion exchange group with potassium or sodium nitrate and ammonium chloride.

TABLE 105.

Components	Explosives		
	Charbrite 418	Charbrite 4/50	Kempoxite 1
Nitroglycerine and Nitroglycol	9.5	9.5	12.0
KNO_3	58.25	55.25	–
$Na NO_3$	–	–	48.0
NH_4Cl	30.0	28.0	30.3
Ammonium Oxalate	–	5	6.5
Hydrophobic compounds	2.25	2.25	–
Calcium stearate	–	–	0.35
Guhr	–	–	2.0
Cellulose	–	–	0.7
Oxygen balance %0	+8%	+5.5%	+4.3%

WATER–GEL (SLURRY) EXPLOSIVES

The last twenty years have shown a rapid increase in the use of Water–gel (Slurry) Explosives in commercial explosives.

The consumption of 2·5 millions of pounds in 1958 grew to over 460 and 400 millions of pounds in 1979 and 1980 respectively [10] in the U.S.A. They were originally used in metal mining (iron-ore open-pit operations) on a large scale, and until now metal mining, quarrying and non-metal mining remain the main consumers of water–gel explosives.

Two excellent reviews have appeared: on the earlier history [72, 73] and recent development of slurry (water–gel) explosives [74].

History

Abel as early as 1874 [75], Kast [76] and T. Urbański *et al.* [77, 78] proved that the presence of water in high explosives increased the rate of detonation (see Fig. 43 and Tables 50 and 62). This found limited practical application in the use of nitrocellulose with water in demolition cartridges [75, 76]. Streng and Kirshenbaum [79] obtained a patent for an explosive composed of ammonium nitrate aqueous solution with aluminium powder. In Sweden Wetterholm *et al.* [80] obtained a patent in 1957 which claimed: 'an oxygen balanced plastic safety explosive characterized by its main ingredients being 20–45% of a high velocity, high brisant explosive, oxygen delivering inorganic salts mixed in a gel of water and a hydrophilic colloid with an amount of water between 3–25%'. The explosive 'Securit' contained 34% DiTEU (*N,N*-bis-β, β, β-trinitroethyl) urea (Chapter VIII, p. 247) 54% NH_4NO_3 and $Ca(NO_3)_2$, 0.8% rice starch, 5.2% glycol and 6.5% water. The explosive showed the rate of detonation 6100 m/s, gap test of diameter, 25 mm was 4–5 cm, critical diameter in a glass tube was 11 mm. Industrial manufacture was not fulfilled (1950) owing to the introduction of the successful AN–FO explosives.

On the contrary, in the United States the 'slurry explosives' developed by Cook [81, 82] and tested in the Iron Ore Co., in Canada in 1957 was quickly accepted in open pit work. The original composition by Cook and Farnam [81] was 25% coarse TNT, 55% NH_4NO_3 or NH_4NO_3 (35–45%) and $NaNO_3$ (10–20%) 20% H_2O with added guar gum as a thickening agent. The addition of the thickening agent was a considerable improvement as it prevented segregation of the ingredients. Guar gum is a polysaccharide: galacto-mannan [83].

Also another patent appeared at the same time by Hardel and Bjork [84] who used aluminium powder as a sensitizer (instead of TNT).

It was soon recognized that the presence of tiny air-bubbles in the slurry was a very good sensitizer. The bubbles adhere to TNT particles or Al powder and help detonation by creating hot spots by adiabatic compression.

Another kind of early slurry was that developed by Gehrig of Atlas Chemical Industries [85]. It consisted of a saturated solution of ammonium nitrate in nitric acid of 60–70% HNO_3 and some organic substances which are not attacked by nitric acid, for example, vinyl polymers. However handling of the solution with nitric acid is difficult and can be dangerous. A fire occurred in a factory in Rourkela (India) in 1972 through spilling nitric acid slurry on wooden boards [86].

The advantages of slurry explosives were summarized by Mahadevan [74] as below:

1. By dissolution, water brings the ingredients into close contact with each other.
2. It provides a continuous medium through which a detonation wave passes.
3. It desensitizes the explosive against fire, sparks, impact and friction thereby decreasing hazards associated with storage and handling.
4. Water is believed to increase the energy of the explosive by taking part in the reaction at the time of explosion especially when Al is present in the composition.
5. It affects the products of detonation and suppresses the formation of toxic gases: carbon monoxide and oxides of nitrogen.
6. It has a pronounced effect on the 'Coke Oven' reaction $2\,CO \rightarrow C + CO_2$ which is very important in preventing dissociation of energetic products of detonation such as H_2O and CO_2.
7. Low percentage of water presents problems on storage: the explosive becomes hard and grainy due to the crystallization of inorganic oxidizer salts on the contrary a higher percentage of water decreases the sensitivity as well as the strength. According to Cook, 1% increase in water lowers the strength of the slurry by *ca.* 1.7%. Thus an optimum percentage of water is in the range of 8–20%.
9. Water acts as a coolant and offers a perspective of using water–gel explosives in underground gassy coal mines.

Cross-linking Agents

One of the draw-backs of early compositions was the low viscosity of the solution and hence the ease of segregation and loss of air-bubbles. A deterioration in performance was observed on storage. A significant achievement consisted in increasing the viscosity of guar gum by adding cross-linking gel forming agents.

The first cross-linking agents were borax and other boron compounds, antimony compounds e.g. ammonium pyroantimonate, potassium antimony tartrate followed by adding a dichromate, that is oxidation of trivalent to pentavalent antimony was found to give an efficient cross-linking agent [74].

Semi-synthetic and synthetic polymers are also used as thickening agents. Such are carboxymethyl cellulose [87, 6] and polyacrylamide [73] respectively.

Surface Active and Emulsifying Agents

Surface active agents (surfactants) improve the dispersion of ingredients and consistency of slurry. According to Hiroshi *et al.* [88] by adding small amounts of alkali metal salts of alkyldiphenyl ether disulphonic acid a slurry explosive was obtained which can be initiated with a No. 6 cap without adding sensitizers. Also alkali metal salts of sulphuric acid esters of higher aliphatic alcohols, of aromatic sulphonic acids are good surfactants and improve the detonability of slurry explosives. Sorbitol monooleate was recommended [74] as the emulsifier.

Oxygen Carriers

In addition ammonium nitrate, sodium nitrate and calcium nitrate are added to slurry explosives. A mixture of calcium nitrate and sulphur [89] seems to be particularly efficient. Calcium nitrate makes slurry more resistant to low temperature and the explosive can withstand the temperature of −12°C. Ammonium perchlorate can also be used [72], but does not seem to get a wider application.

Aluminium

The addition of aluminium powder in a form of foil, flakes or granules can make slurry without nitro compounds. The patent by Davis, Fassnacht, Kirst and Noran [90] gives slurry explosives composed of ammonium and sodium nitrate, aluminium and water. An emulsifier is added to help the presence of air bubbles. The fact that aluminium can react with the strongly oxidizing ingredients of the explosive mixture can be dangerous.

Aluminium in the presence of water in a strongly oxidizing medium can make the explosive deteriorate and also create danger through heating and gassing. To avoid the reaction of aluminium coating is recommended of Al particles, with stearic, palmitic and oleic acids [74]. Flakes and dust of aluminium posed handling problems as it resists wetting of aqueous medium. Mahadevan and Varadarajan [91] solved the problem by wetting aluminium with ethylene glycol and adding such paste to the mixture.

Alkylamine Nitrates

A number of patents (e.g. by Dunglinson [92]) disclosed that by adding alkylamine nitrates to slurry a great increase in sensitivity could be achieved. Particularly efficient is methylamine nitrate, as disclosed by Frederic [93] and at present Du Pont Co. and I.C.I. are using methylamine nitrate as an ingredient of their slurry explosives [74]. Du Pont issued the explosive under the trade name 'Tovex' [73]. Methylamine nitrate is made by reacting methylamine with concentrated nitric acid (66%) free of nitrous acid (Vol. II, p. 465). It is important that nitric acid is free of nitric oxides which would give side reactions (e.g. diazotization) of methylamine.

There are no remaining problems in formulating water–gels which will perform well in any construction or mining operations under all climatic conditions. Although water-gels are not cheaper than NG-based explosives, manufacturers and customers prefer to use these explosives because of lesser hazards involved in manufacture, storage, transportation and handling.

The slurries can be 'tailor made' to suit individual strate conditions, thus enabling maximum burden to be achieved with the best fragmentation resulting in the reduction of the overall cost of mining. Maximum coupling and hence maximum utilization of energy released to break the rock can be achieved by using water–gels especially pourables. At present the only advantage of NG-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water–gels have replaced NG-based explosives. The present trends indicate that the former may replace the latter.

Compositions of a few slurry explosives in different countries are given in Tables 106–109.

In Germany Wasag Chemie Sythen G.m.b.H. factories are producing Wasagel explosives with 12% or more water. Mark IK is a non-freezing gel.

Dynamit Nobel AG are making Dynagel mark 1, 2, 3, P1 and P2. All the above explosives are with negative oxygen balance and can be used for open-cast work only. For their properties – see Meyer [69].

Slurry explosives for open-cast work in U.S.S.R. comprise also granulated TNT ('Granulotol') and a granulated mixture of TNT with 15% Al ('Alumotol').

Table 108 gives a comparison of the properties of Granulotol dry and with water.

The heat of detonation of 'Alumotol' is by *ca.* 35% higher than of 'Granulotol' and so is lead block expansion.

TABLE 106. Water-gel blasting agent (SBA) and Slurry Explosives (SE) made in U.S.A. [72]

Components	SBA Al	SE	SE
NH_4NO_3 } $NaNO_3$ }	49	39	–
$NaClO_4$	–	–	39
Al	35	25	25
H_2O	15	15	15
Thickener	1	1	1
Density	1.45	1.60	1.88
Relative crater volume (TNT/Al 80/20 = 1)	1.22	1.22	1.73

TABLE 107. Water-gel (slurry) explosives made by Du Pont of Canada [73]

Components	Trade Names			
	Tovex 20	Tovex 40	Tovex A–4	Tovan 30
TNT	20	40	20	–
NH_4NO_3	49	27	37	48
$NaNO_3$	12	15	10	15
Al	–	–	15 (granules)	15 (flake)
Water	15	15	15	17
Other (Thickening, surface active agents etc.)	4	3	3	5
Properties				
Density	1.40	1.40	1.42	1.27
Rate of detonation V m/s unconfined, 5 in. dia	4600	5500	4730	
Confined in steel 5 in. dia	4680	5865	5350	
Calculated: V m/s	5000	5850	5500	5000
Heat of explosion kcal/kg	760	780	1125	1210
Gas volume l/kg	830	850	740	670

Japanese slurry explosives are all based on Du Pont, Hercules or IRECO Chemicals.

Sunvex 100A, 200 and 220 contain methylamine nitrate. Energel MA-7 contains ethanolamine mononitrate. IRECO explosives are sensitized with Al.

The following are slurry explosives used in Sweden [67]: Reomex A (aluminized and methyl nitrate sensitized), Reomex B (methyl nitrate sensitized) and Reolit C (TNT sensitized) gels. Their oxygen balance is –0.35, +1.43 and –1.75 respectively, and the rate of detonation 4000–5000 m/s, however no exact com-

TABLE 108. Akvatols, Akvanals and Akvanits
(Slurry explosives used in U.S.S.R. [6])

Components			Akvatol		Akvanal		Akvanit	
	65/35	AB	MG	M–15	No. 1	2	3L	16
NH_4NO_3	63	51	26.5	58.5	57	44.2	25.5	53
$NaNO_3$	–	–	20	–	–	–	32	–
$Ca(NO_3)_2$	–	–	–	–	10	7.4	–	10
TNT	34	28	–	25	20	5	30	29
Cyclonite	–	–	–	–	–	35	–	–
Al	–	–	–	15	5	–	–	–
Alumatol 75/25	–	–	40	–	–	–	–	–
Na-carboxy-methylcellulose	3	–	–	1.5	1.0	1.1	0.5	1.0
Borax	–	–	–	0.02–0.04*	–	–	–	–
Polyacrylamide	–	2	–	–	–	–	–	–
Guar gum	–	–	1.5	–	–	–	–	–
Mineral Jelly	–	–	–	–	–	0.8	–	–
Water	15*	14	12	15*	6	6.5	12	6
Antifreeze	–	5	–	–	–	–	–	–
Sulphite cellulose extract	–	–	–	–	1.0	–	–	–

* Over 100%.

Lead block expansion of the above explosives is from 310 cm^3 (Akvanit No. 1) to 480 cm^3 (M–15) and the rate of detonation is 4500–5500 m/s. The density: 1.30–1.55.

TABLE 109. Properties of dry and slurried TNT
(U.S.S.R.) [6]

	Dry	Slurried
Heat of detonation kcal/kg	825–870	1000
Volume of gases l/kg	745	895
Lead block expansion cm^3	285–295	320
Rate of detonation m/s	4500–5000	5500–5700
Critical diameter mm in open	60–80	–

position was given. Methylamine nitrate is a very good sensitizer of slurry explosives. Owing to this fact T. Urbański suggested, and took part in, developing at IDL Chemicals Ltd, Hyderabad, India [94] the manufacture of methylamine nitrate by the Plöchl reaction, that is, by reacting ammonium nitrate solution with formaldehyde. A small proportion of dimethylamine and a still smaller proportion of trimethylamine nitrate is produced in this reaction, and the reaction requires special conditions because it occurs in an oxidizing medium of ammonium nitrate.

Relatively recent information [112] is that Du Pont de Nemours stopped its dynamite manufacture at the end of 1976. Dynamites have been replaced by cartridges of 'Tovex' explosives with amine nitrate sensitizer and without nitroglycerine.

Although methylamine nitrate was considered to be a relatively safe and – in addition – is present in an aqueous solution precautions should be taken with regards to the problem of safety of handling the solution. The explosion of two tank cars loaded with 86% solution of methylamine nitrate occurred in Potomac River (U.S.A.) in 1976. The explosion was probably due to friction in a pump [86]. An important paper by Persson, Jerberyd and Almgren [111] established that methylamine nitrate slurry explosives of the Swedish type of pumpable water–gel (Bulkreomex) could decompose when piston velocity increased above 20 m/s.

Gas Bubbles

The role of gas bubbles in explosives has already been discussed (pp. 298, 547). Goffart [96] described the importance of gas bubbles which increase the cup sensitivity of slurry explosives containing aluminium dust. However, the presence of gas bubbles of course reduces the density and subsequently the rate of detonation, for example a density of 1.33 falls to 0.83 and the rate of detonation from 3600 m/s to 2710 m/s (for a diameter of 36 mm).

The critical diameter of slurry explosives was determined by Michot and Bigourd [97]. The smallest critical diameter (22 mm) is shown by slurry with Al (density 0.95) and with methylamine nitrate (density 1.00). Also the method of determining the critical diameter has been given [98].

Permitted Slurries

Van Dolah, Hay *et al.* [99, 100] developed permitted slurry explosives with sodium chloride. Mahadevan [101] studied the stability and performance of permissible slurries, and Mahadevan and Varadarajan [91] described the commercial production of permitted slurries of small diameter cartridges.

Slurries with High Explosives

TNT was a common ingredient of slurry explosives of the 'Tovex' type made by Du Pont of Canada (see Table 107) [73]. PETN and RDX slurries were developed by T. Urbański [95]. The method consisted in dissolving pentaerythritol and hexamethylene-tetramine in nitric acid (d. 1.50) and neutralizing with ammonia or ammonium carbonate the solution containing some suspended PETN and RDX. A solution of ammonium nitrate in water with suspension of the above explosives resulted.

There is however a tendency to avoid incorporating typical high explosives into slurries owing to their high cost and sensitivity to impact and friction.

Ethylene glycol mononitrate was in use in Canada and an accident occurred in Beloeil in 1975 [86]. As glycol mononitrate was considered to be safe to handle no special precautions were taken and it was pumped with two Moyno pumps. The detonation which destroyed the factory probably started through friction in a pump.

Composition of Slurries with Nitroglycerine based Explosives

A comparison was made by Mahadevan [74] of slurries with 'classical' nitroglycerine explosives as follows:

> "At present the only advantage of nitroglycerine-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water–gels have replaced nitroglycerine-based explosives."

FIG. 100. Nonel 1-tube (detonating fuse) showing a thin layer of explosive inside the plastic tube (Courtesy Nitro Nobel A.B., Gyttorp, Sweden).

NONEL DETONATING FUSE

Among the most important inventions in the field of accessories to mining explosives is the Nonel Detonating Fuse ingeniously invented by P. A. Persson at Nitro Nobel A.B. [113].

It is composed of a thick walled polyethylene tube sprayed inside with a small amount of a highly sensitive and strong explosive such as Octogene (HMX), Cyclonite (RDX) or PETN. It is based on the fact that a shock wave travels along the tube with a higher velocity than the detonation wave. Figure 100 gives a cross-section of the Nonel tube.

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APPENDIX

METHODS OF DETERMINING THE ABILITY OF EXPLOSIVES TO DEFLAGRATE

Methods of determining the ability of explosives to deflagrate were introduced in 1934 by Audibert and Delmas [1]. It consisted determining whether an explosive can be subjected to burning or exploding under the flame produced by ignition charges.

A general scheme was developed in different countries which consists in the following method: an explosive is confined in a steel tube of different dimensions, viz.:

length	200–1370 mm
diameter	38–90 mm
wall thickness	3–20 mm

The tube is closed on both sides. One of the closing plaques is provided with a nozzle of different diameters, e.g. from 1 to 20 mm. Another one is covered inside by an inert substance, such as sand. The initiation of the explosive is usually made by black powder or an explosive mixed with coal-dust.

The minimum diameter of the nozzle which produces a deflagration is determined and serves as a measure of the ability of the explosive to deflagrate.

Another criterion is the proportion of coal-dust added to the examined explosive. In Poland the explosive is mixed with coal-dust (up to 55%). The minimum addition of coal-dust which gives a deflagration is 17–28%. Pure ammonium nitrate explosives do not deflagrate.

Further description of the methods of determining a deflagration is outside the scope of this book. They are fully described by Charewicz [2].

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CHAPTER 20

THE MANUFACTURE OF COMMERCIAL (MINING) EXPLOSIVES

(Vol. III, p. 498)

Little can be added to first steps of manufacturing mining explosives, such as drying, milling and mixing of ingredients of mining explosives (Vol. III, pp. 498–503). Disk mixers (Vol. III, p. 504, Fig. 167), edge runners (Vol. III, p. 350, Figs 93, 94) and Werner-Pfleiderer kneaders (Vol. III, pp. 586–7, Figs 206–209) are still in use for mixing ammonium nitrate explosives without nitroglycerine.

Those with a small amount of nitroglycerine (4–6%) can be mixed in Werner-Pfleiderer and in Drais kneaders (Vol. III, pp. 512–514, Figs. 173–175). The latter are particularly suitable for making explosives with a higher content of nitroglycerine.

PLANETARY MIXERS

The typical planetary mixer is a Drais kneader the most commonly used type is with two bowls pivoting around an axle. While one of the bowls is being emptied or filled, the other one is under the stirrers. The capacity of the bowl is of about 500 kg of dynamite. More recently Drais has built a machine of 500 l useful capacity consisting of four instead of two pillars (Fig. 101).

Another kind of planetary mixer of a smaller capacity (250 kg) was developed by Biazzi S.A., Vevey (Fig. 102) [1]. The main characteristics are the light structure of aluminium, the particular disposition of blades which makes it possible to avoid a foreign body being caught into the mass and wedged between the blades and the interior of the bowl.

The stirrers revolve one around the other at 17 rpm and rotate around their own axis at 45 rpm. The speed can be changed and the mixing time can be kept between 4 and 8 min. At a lower speed the danger of explosion is smaller. The stirring can be clockwise or anticlockwise. The machine is stopped and the stirrers are raised automatically by means of a timing device.

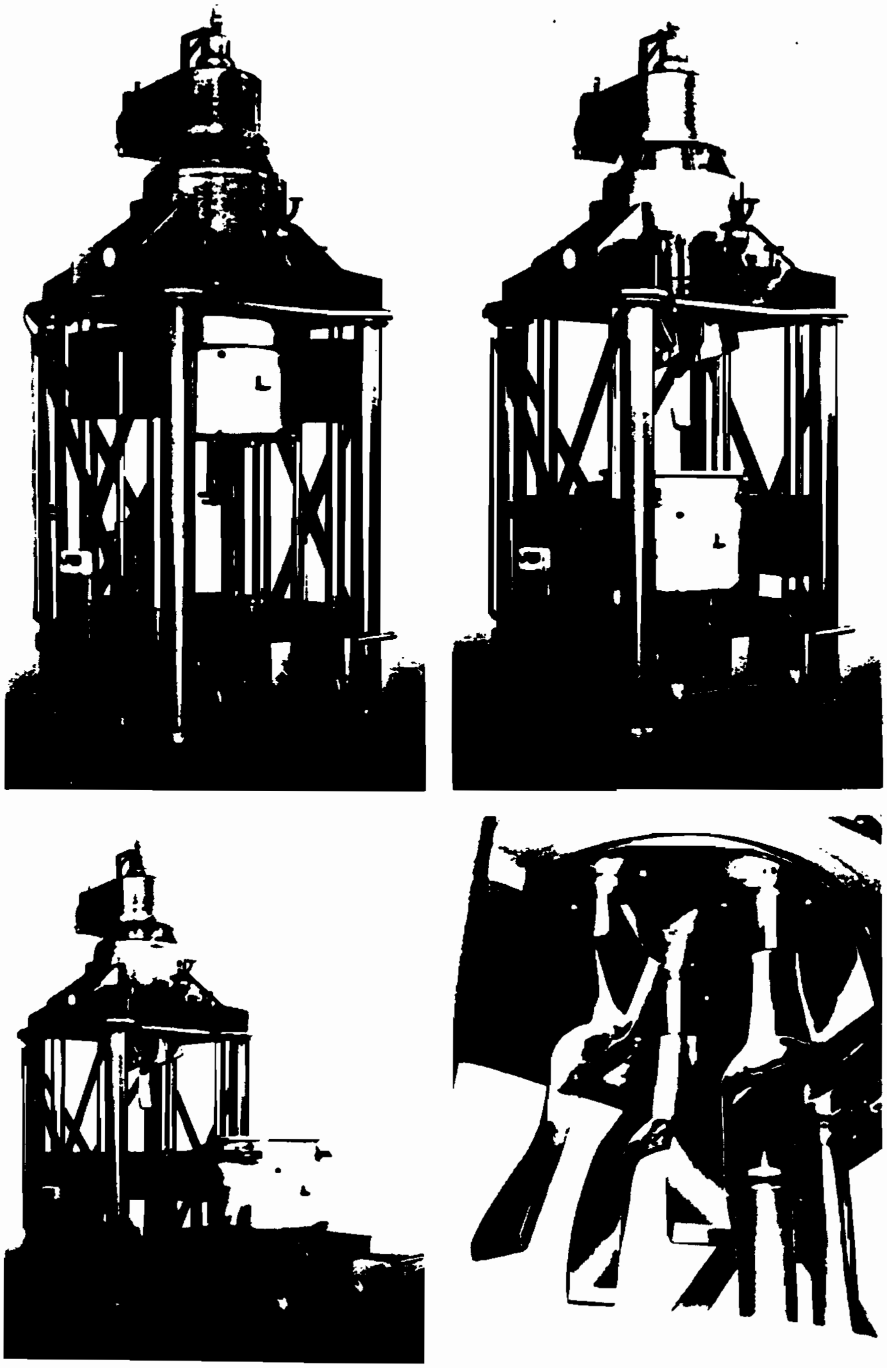

FIG. 101. New design for a Drais Planetary Mixer (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldorf, FRG).

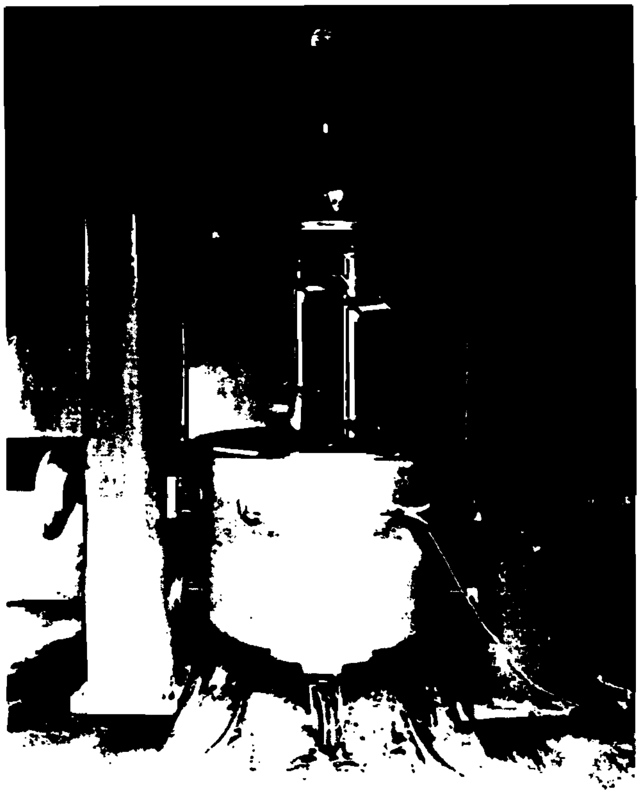

FIG. 102. Planetary mixer by Biazzi (Courtesy Biazzi S.A., Vevey, Switzerland). Earth connection of the bowl can be seen.

Although the design of planetary mixers excludes friction, a few explosions have occurred [2]. Most of them were due to the presence of foreign bodies in the bowl, and a few accidents were due to hand stirring the mixtures, contrary to instructions.

Also a few accidents with Werner-Pfleiderer mixers have been described [2] mostly due to the accidental presence of foreign bodies.

Another kind of explosives mixer 'Tellex Mixer' has recently been developed by Fr. Niepmann, G.m.b.H., Gevelsberg, FRG [3]. The mixing bowl is of steel alloy and consists of two troughs in which mixing can be made of powder, semi-gelatinous and gelatinous explosives, as well as AN–FO and slurry mixtures. The capacity of the troughs is 180–700 kg.

Two spiral stirrers guarantee good mixing (Figs 103a, b).

Mixing lasts 8–10 min and remote control assures the safety of personnel (Fig. 104).

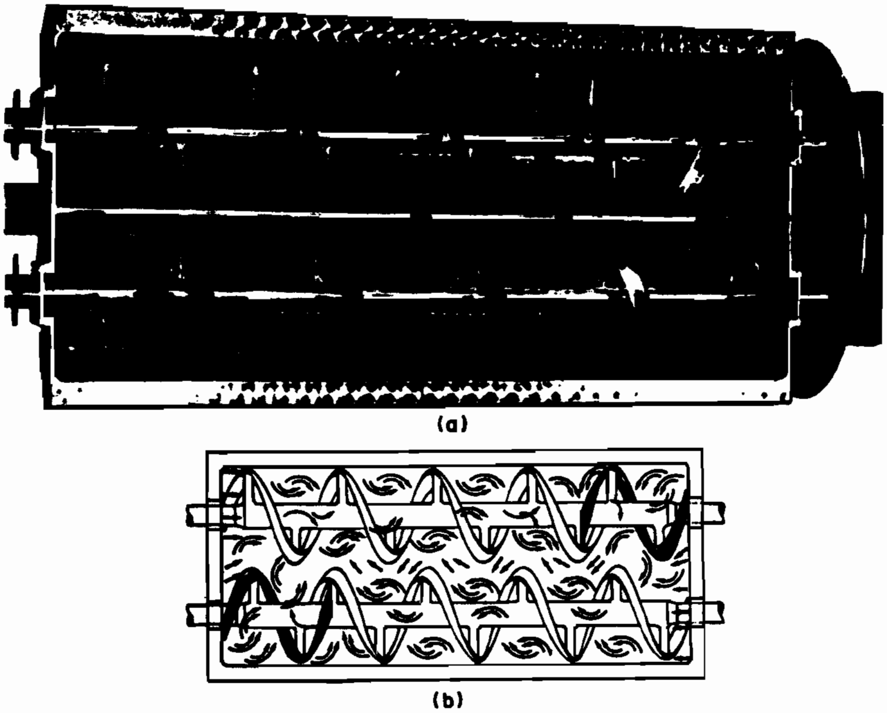

FIG. 103. Tellex explosives mixer by Niepmann (Courtesy Niepmann A.G. Maschinenfabrik, Walchwill/ZG., Switzerland) (a) View from above; (b) Diagram of functioning of stirrers.

CARTRIDGING

Maschinenfabrik Fr. Niepmann G.m.b.H. & Co., Gevelsberg, FRG specializes in making cartridging machines for explosives. A diagram of an early version of a cartridging machine is given in Vol. III, pp. 517–8, Fig. 179. Two modern Niepmann cartridging machines will be described here.

Figure 105 depicts 'Cartex' for cartridging powder-explosives, a cartridging machine which makes 9 cartridges (there are also models making 12 cartridges) [4].

The explosive is fed by screws into the open end of the paper tubes. When shells have been filled, the screws stop automatically, then a brief reverse rotation prevents a surplus feed. The filled tubes travel to the folding machinery where they are closed before being conveyed to the paraffining station, if necessary. The operation is controlled at two points: by manual control inside the cartridging room and by a remote control panel in the control room.

Machines of this type can make cartridges of 20–40 mm diameter and 90–254 mm length, with a yield of 100–180 cartridges per minute.

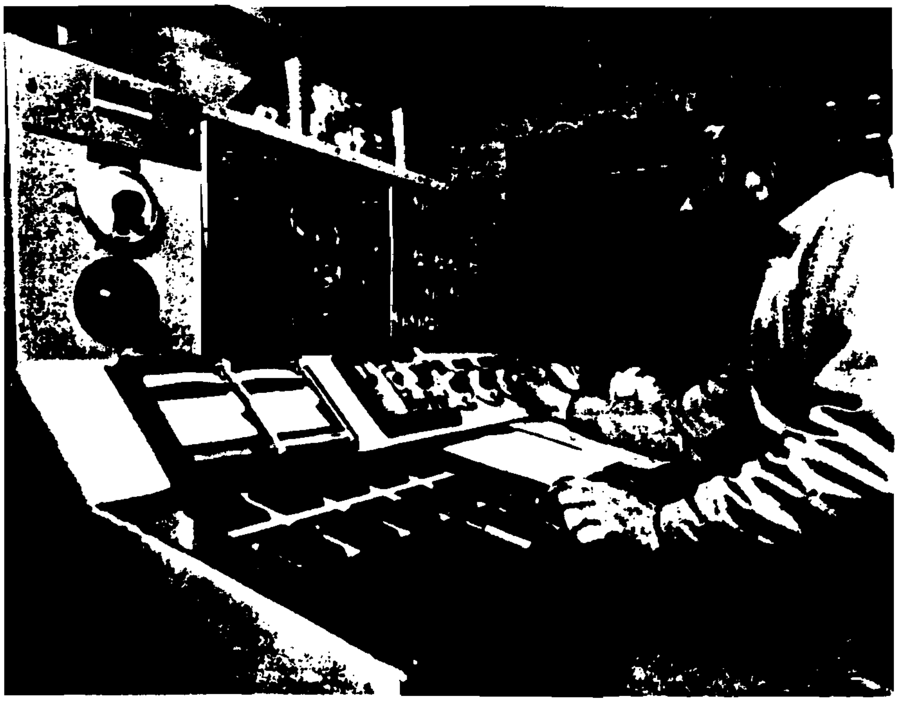

FIG. 104. Control room of mixing explosives at Kemira (Courtesy Kemira OY, Vihtavuori, Finland).

Figure 106 depicts a cartridging machine LD-Ex 701 for gelatinous explosives [5]. Large diameter cartridges can be made: 50–125 mm diameter and 300–800 mm length. The hopper is loaded with an explosive. Feed rollers and transfer screws convey the material to the filling station. Plastic film from a supply reel is formed into tube, and the longitudinal seam is sealed. The explosive is fed into the casing until a desired length has been reached. The filling screw is stopped, the tube is pulled away and wire clips are applied to close the cartridge and the film is cut between the two clips. Cartridge length is adjustable. The machine can make 10–15 cartridges/minute.

Although the Niepmann machines are safe to handle, an accident occurred as described by Biasutti [2] in Rego da Amoreira, Portugal. As is usual in such accidents, it was due to the presence of a foreign metal object in gelatinous explosive with 33% nitroglycerine.

AN–FO

The methods of making AN–FO mixtures were described in Vol. III, pp. 508–510. In the early stages of AN–FO manufacture no necessary precautions

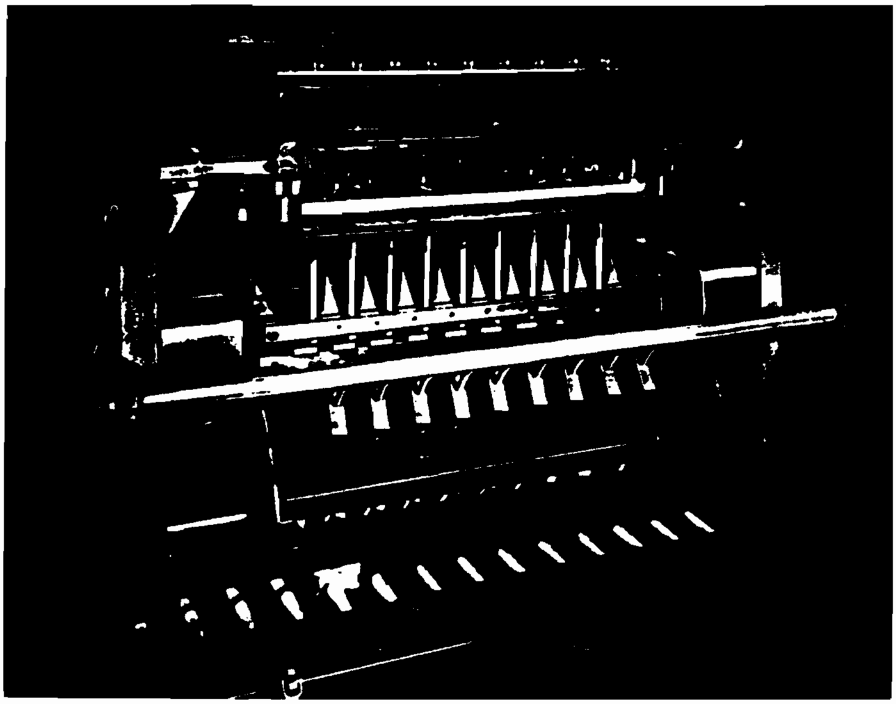

FIG. 105. Niepmann automatic filling and closing machine with 9 filling tubes (Courtesy Maschinenfabrik Fr. Niepmann G.m.b.H. and Co., D-582 Gevelsberg, FRG).

were taken AN–FO being erroneously considered to be a safe mixture. A huge accident at Norton, Virginia, U.S.A. (Vol. III, p. 508) compelled the authorities to issue instructions on the manufacture and handling of AN–FO, a detailed description of the accident can be found in the book by Biasutti [2]. The accident started when the mixture caught fire, probably from welders working in the premises. The fire was followed by several explosions which produced extensive damage. Since then AN–FO has been recognized as a conventional explosive and all regulations valid for explosives, should be applied as regards manufacture, handling, transportation and storage of AN–FO.

The methods for making and applying AN–FO for blasting have been given by Schiele [6].

Two modern methods developed by Nitro Nobel in Sweden are depicted in Figs 107 and 108. Portanol (Fig. 107) is a pneumatic ejector developed for the efficient charging of AN–FO made from ammonium nitrate prills. It is based on the ejector principle, that is, the blasting agent is sucked from the container and blown through a hose into the bore-hole.

Anol (Fig. 108) is a compressed air unit for charging AN–FO into shot-holes of 25–150 mm diameter.

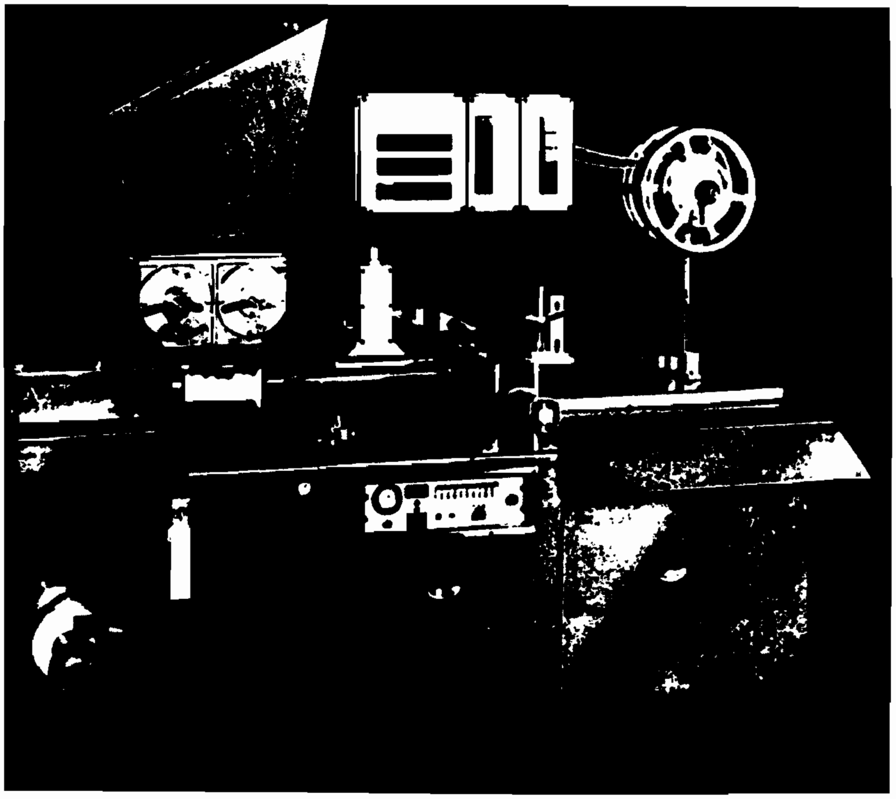

FIG. 106. Explosives packing machine for large diameter cartridges (Courtesy Maschinenfabrik Fr. Niepmann G.m.b.H. and Co., D-582 Gevelsberg, FRG).

FIG. 107. 'Portanol' ejector charger for prilled AN–FO (Courtesy Dr J. Hansson and Mr Bengt Ljung of Nitro Nobel Mec. Stockholm).

FIG. 108. 'Anol' for charging AN–FO (Courtesy Dr Jan Hansson and Mr Bengt Ljung of Nitro Nobel Mec. Stockholm)

It is important that the vital parts of the apparatus are made of stainless steel owing to the fact that AN–FO is highly corrosive. The charging hose is antistatic and electrically semi-conductive to avoid charging with static electricity.

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CHAPTER 21

LIQUID EXPLOSIVES

LIQUID OXYGEN EXPLOSIVES (OXYLIQUITS) (LOX) (Vol. III, p. 491)

Liquid oxygen explosives were widely used in Germany during World War I owing to a shortage of nitric acid and hence – aromatic nitro compounds. Shortly after World War I (Vol. III, p. 493) their use was limited. This was partly due to a number of fatal accidents, these explosives are little used today in most countries [1]. The use of LOX declined because of the introduction of AN–FO and Slurry explosives [2].

LIQUID ROCKET PROPELLANTS–PROPERGOLS (Vol. III, p. 291)

A few monographs and collective volumes have been published and should be consulted for further information on this expanding and very wide subject [3–9, 35]. The history of liquid propellants is given by Roth [7] based on the description by Malina and Truaux in a collective volume [8]. The scope of the science of Liquid Propellants is not limited to rocket propulsion but also embraces jet propulsion of engines and their design. This is outside the scope of this book. Subsequently only the information strictly connected with rocket propulsion will be given here.

Mono- and Bipropellants

a. Monopropellants are composed of substances which contain in one molecule both combustible and oxidizer moiety and possess explosive properties. Such are: nitromethane, methyl nitrate described already in Vol. I and II respectively and in Chapters VIII, X (this volume). They will not be discussed here.

b. Bipropellants are composed of two components: a fuel and a liquid oxidizer. Separately neither of them is explosive, but their mixture possesses burning and explosive properties. The liquids can be individual compounds or mixtures, and usually belong to hypergolic mixtures (Vol. III, p. 291), that is, they react spontaneously after a short induction period followed by mixing. The term 'Hypergolicity' is now in use for 'self-ignitability'. Non-hypergolic systems are not currently much in use [9].

The following were groups of compounds used as fuels: hydrocarbons, amines, hydrazines, boranes and as oxidizers: nitric acid, nitrogen oxides, hydrogen peroxide, liquid oxygen, halogens.

A few requirements are posed with regard to the stability of the components, their toxicity, ease of handling and cost of manufacture. From that point of view some ingredients originally suggested could not be accepted, such as liquid ozone which proved to be too sensitive to handle.

Cryogenic and Storable Components

Liquid hydrogen is a typical cryogenic fuel and oxygen and fluorine are cryogenic oxidizers. The latter is a more energetic oxidizing agent than oxygen and also oxidizers containing active fluorine atoms. Thus oxygen difluoride (OF_2) and chlorine trifluoride (ClF_3) (Vol. III, p. 312) are more energetic and reactive than oxygen containing oxidizers such as nitric acid, hydrogen peroxide (98%), dinitrogen tetroxide.

The energetic advantages of cryogenic fuel and oxidizers are visible from their performance in terms of specific impulse I_s as compared with storable components:

	I_s
Cryogenic	
hydrogen and fluoride	410
hydrogen and oxygen	391
Storable	
hydrazine and nitrogen tetroxide	292
methylhydrazine and chlorine trifluoride	284

Storable liquid propellants now receive greater attention than cryogenics. Storability refers to a liquid which can be kept for a long time at ambient temperature in standard containers without any significant loss of material.

The following are requirements applied to storable liquids [10]:

1. the freezing point should be sufficiently low to assure the liquid state under different climatic conditions. Also they should possess:
2. high density,
3. low vapour pressure,
4. relatively low viscosity.

They should not be excessively toxic, corrosive, reactive with air or thermally unstable. Their performance should be as high as possible and this is obviously limited to particular chemical structures. Subsequently blends were introduced for example, 50/50 hydrazine/unsym-dimethylhydrazine (UDMH), or UDMH with acetonitrile and diethylenetriamine (DETA). On UDMH see Vol. III, p. 308.

Most storable energetic oxidizers are very reactive, toxic and not very stable (e.g. ClF_3, N_2O_4, H_2O_2). The corrosive properties of nitric acid: RFNA and WFNA (85 and 97% HNO_3 respectively) are greatly removed by adding 0.5–1.0% HF thus forming IRFNA and IWFNA (inhibited acids) – as pointed out in Vol. III, p. 293 and in Chapter I of the present book. Sometimes a small proportion (*ca.* 1%) of phosphoric acid is also added.

Hypergolic Systems

The above described systems with compounds containing amino groups are hypergolic systems.

Kulkarni [11] gave a list of various compounds hypergolic with WFNA and their induction period according to [12] (Table 110).

The data for hydrazine [13] and UDMH [14] are given in Table 111.

TABLE 110.

Compound	Induction period sec.
Ethylamine	2.03
Propylamine	1.73
iso-Propylamine	0.94
sec-Butylamine	0.63
Diethylamine	0.45
Dipropylamine	0.17
Di-iso-Propylamine	0.15
Triethylamine	0.07
Tripropylamine	0.05
Ethanolamine	0.43
Ethylenediamine	0.09

TABLE 111.

Compound	Agarmond	Induction period sec	Reference
Hydrazine	RFNA	0.003	[13]
Hydrazine	HNO_3 (98%)	0.005	
UDMH	HNO_3 (98%)	0.012	[14]

Capener [9] and other sources [7, 24] give a wide list of hypergolic systems which can be summarized as follows:

Oxidizers: RFNA, WFNA, N_2O_4, N_2O_4 + NO (MON), Liquid oxygen (LOX, LO_2), Ozone, H_2O_2, Fluorine, Oxygen/Fluorine (Flox 30 and 70 with 70% of fluorine respectively), Fluorine chloride (ClF_3 – Vol. III, p. 312), Perchloric acid (Vol. III, p. 313), Perchloryl Fluoride (ClO_3F – Vol. II, p. 468, Vol. III, p. 313), Tetrafluorohydrazine (N_2F_4), Oxygen difluoride OF_2 [21–23], Bromine pentafluoride (BrF_5), Tetranitromethane (Vol. I, p. 588 and Chapter VIII, this volume).

There is currently a tendency to use oxygen fluorine and its compounds more widely.

Fuels: Diethylenetriamine (DETA), $(NH_2C_2H_4)_2NH$, Hydrazine, Monomethylhydrazine (NHM), Unsymmetrical Dimethylhydrazine (UDMH, Vol. III, p. 308), Terpenes, also non-hypergolic fuels JP-4 and JP-5 are in use.

Other composite fuels which are in use are:

MAF 1 a mixture of 50% DETA, 40% UDMH and 10% Acetonitride, MAF 3: 20% UDMH and 80% DETA, MAF 4 (Hydyne or U-DETA): 60% UDMH + 40% DETA, N_2H_4-UDMH: a mixture 50/50 of two components. Hydrodyne V: 75% hydrazine and 25% MMH, JP-X: 60% JP-4 and 40% UDMH.

Practical applications have been found for most of these compounds with some exceptions such as: liquid ozone as it is considered to be too difficult to handle, the only probable form of ozone safe enough is its mixture with oxygen (Vol. III, p. 309).

Intensive research is still being carried out to find the best oxidizer and fuel. Capener [9] gives a few examples of the most promising systems, they are collected in Tables 112–116. Roth [7] reported the most commonly used liquid propellants – Table 117.

Further information has been presented by Silverman and Constantine [24], who have described non-hypergolic mixtures of liquid oxygen with RP-1 (a hydrocarbon blend), hydrogen, ammonia, ethanol; hydrogen peroxide with hydrocarbons JP-4 and JP-5; IRFNA with JP-4. They also described hypergolic mixtures, such as: IRFNA with JP-X, UDMH, MAF-1, -3 and -4, aniline and furfurol; IWFNA with turpentine; N_2O_4 and hydrazine with UDMH, MMH, hydrazine with MMH, MON with MMH and UDMH.

TABLE 112. Propellants with RFNA
(composition: 84.6% HNO_3, 13.4% N_2O_4, 2% H_2O)

Enthalpy of formation RFNA – $\Delta H_f = 41.0$ kcal/mol
Density 1.57 at 25°C
m.p. −49°C
b.p. 66°C

Fuel	Oxidizer wt %	Specific impulse I_s max sec
B_5H_9	77	298
Hydrazine	60	278
MMH	71	278
UDMH	76	272

TABLE 113. Propellants with N_2O_4

Enthalpy of formation N_2O_4 – $\Delta H_f = 5.4$ kcal/mol
Density 1.43 at 25°C
m.p. −11.2°C
b.p. 21°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	84	342
B_5H_9	77	306
Hydrazine	57	291
MMH	68.5	288
UDMH	72	286
DETA	74	278

TABLE 114. Propellants with H_2O_2 (100%)

Enthalpy of formation H_2O_2 – $\Delta H_f = 44.8$ kcal/mol
Density 1.44

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	88	322
B_5H_9	73	316
Hydrazine	67	286
UDMH	81	283

TABLE 115. Propellants with fluorine

Enthalpy of formation of F_2 – $\Delta H_f = 3.47$ kcal/mol at −188°C
Density 1.51 at −188°C
m.p. −219.6°C
b.p. −188°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	89	410
B_5H_9	82	360
Hydrazine	69	363
UDMH	71	344
NH_3	77	357

TABLE 116. Chlorine trifluoride

Enthalpy of formation of ClF_3 (liquid), $-\Delta H_f = 44.4$ kcal/mol

Density 1.81 at 25°C
m.p. −82.6°C
b.p. 11.3°C

Fuel	Oxidizer wt %	Specific Impulse I_s (max) sec
H_2	92	318
B_5H_9	88	290
Hydrazine	73	293
MMH	74	283
UDMH	75	280
DETA	75	267

TABLE 117. Most commonly used liquid propellants (according to Roth [7])

Oxidizer	Fuel	Oxidizer: Fuel ratio	Specific Impulse I_s sec
99% H_2O_2	Hydrazine	1.0	245
LOX	Ethanol	1.5	242
LOX	JP-4	2.2	248
Fluorine	NH_3	2.6	288
Fluorine	Diborane (B_2H_6)	5.0	291
Fluorine	Methanol	2.37	296
Fluorine	Hydrazine	1.98	2.98

Although considered as being storable, oxidizers such as N_2O_4 and ClF_3 are less in use owing to their low boiling points: 21° and 11°C respectively and hence difficulty in handling.

Novel Trends in Liquid Rocket Fuel

In the search for efficient hypergolic fuel various derivatives of furfuryl alcohol have been suggested [14–16]. Some of them have an induction period of the order of 0.020–0.025 sec with 98.5% nitric acid.

Among the fuels reacting with RFNA the following showed hypergolic properties: Schiff's bases [17], furfurylidene aniline and furfuramide [18], Δ^3-carene [19]. Particularly important are the findings of Panda and Kulkarni [20] who described aliphatic, alicyclic and aromatic furfurylidene ketones which are hypergolic with RFNA. The latter had the following composition: 76% HNO_3, 21% N_2O_4, 1% H_3PO_4, 0.3–0.5% HF and 1.7% H_2O.

OXIDIZERS

Oxygen Difluoride (OF_2)

As previously mentioned, oxygen fluorine and fluorine compounds are infrequently used as oxidizers. Oxygen difluoride is a particularly attractive oxidizer. It is denser than the stoichiometric mixture O_2/F_2 and consequently should give a better performance. It was first identified as a product of electrolysis of wet HF as early as 1927 [26]. A detailed description is given by Donohue, Nevitt and Zletz [21] with a yield of 45%, although a yield of 60% was also claimed [27]. Donohue *et al.* found that the yield varies with concentration.

The reaction [21] can be represented by the diagrammatic equation:

$$HF + nH_2O \longrightarrow OF_2 + O_3 + O_2 + H_2. \qquad (1)$$

According to Donohue *et al.* the conversion of HF to OF_2 is 100%.

Oxygen difluoride is a colourless gas of m.p. −224°C, b.p. −145°C [28, 25]. Its density is 1.52 at −145°C [25]. Bisbee, Hamilton, Rushworth, Houser and Gerhauser [23] determined thermochemical parameters of the compounds: the standard $-\Delta H_f^\circ$ was found to be 4.06 kcal/mol and of O–F bond energy −50.7 kcal/mol.

EPR spectrum of OF_2 was also examined [22].

Nitrogen Fluorides

Four nitrogen fluorides are known: NF_3, N_2F_4, N_2F_2 and N_3F, but only NF_3 and N_2F_4 [25, 29] are of real interest in rocket propulsion. They are both cryogenic with b.p. −129° and −73°C respectively. They are relatively resistant to the hydrolytic action of water. So far there is little prospect of practical use owing to the high cost and the yield of toxic decomposition products.

Multicomponent Fuel

Multicomponent systems usually contain aluminium as a component which increases the combustion energy. The stabilization of the system with an insoluble component and aluminium requires that insoluble phases (an insoluble combustible and metal) are uniformly suspended through the liquid phase. According to Beighley, Fish and Anderson [25] two methods were promising:

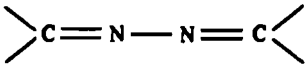
(1) by forming an emulsion,
(2) by forming a gel.

The latter method proved to be more successful. Two types of gelling agents were in use:

(a) silica and acetylenic black,
(b) natural and synthetic hydrophilic polymers.

There is an increasing demand for hydrazine as an excellent fuel. It is commercially made by the Raschig method and has been known since 1907. Its main drawback consists in yielding dilute (2%) solution. The monograph by Audrieth and Ogg (Vol. III, p. 307) is also dedicated to the problem of concentrating the solution. The problem still exists although the classical method was improved by Bayer in Germany. There are environmental problems in disposing of large quantities of by-products and a consumption of large quantities of energy.

According to the Encyclopedia [2] Usine Kuhlmann in France developed a new method which consists in a sequence of reactions: ammonia, hydrogen peroxide and carbonyl compounds (e.g. propione) react in the presence of an amide and a catalytic quantity of phosphate to form an azine intermediate:



The latter hydrolysed quantitatively to hydrazine and carbonyl compound which is recycled. A yield of 75% was claimed.

For gelling hydrazine, MMH, UDMH and their mixtures were used: natural gums, guar gum (applied extensively in slurry explosives – Chapter XIX), gum arabic, locust bean gum, alginates, gelatin, carboxymethyl- and hydroxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone etc. The solid phase should be of course, compatible with the carrier fuel.

The rheological properties of such gels are of importance [10, 25].

The methods of examining the chemical and mechanical stability of propellant systems are described by Tannenbaum and Beardell [10].

POLYMERIZATION OF HYPERGOLIC FUEL

Trent and Zucrow [30] (while studying the hypergolicity of bicyclopentadiene with WFNA) advanced a hypothesis of polymerization reaction of the diene as a pre-ignition reaction. This was substantiated by Panda and Kulkarni [20, 31] through their experiments on self-ignition of several furfurylidone ketones and amines with RFNA. The same authors discovered hypergolicity of unsaturated phenols with RFNA and N_2O_4 [32]. The phenols are able to polymerize. In a series of recent papers Panda and Kulkarni [33] supported their hypothesis experimentally.

ANALYSIS

The analysis of liquid rocket propellants has been described in a monograph by Malone [34]. This is however outside the scope of the present book.

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CHAPTER 22

SMOKELESS POWDER

(Vol. III, p. 528)

Little can be added to the general description of smokeless powder given in Vol. III, although its use is wider than originally described and is not limited to firearms but is extensively used for rocket propulsion.

From the point of view of composition three kinds of smokeless powder can be described: single, double and triple-base powder.

The general characteristics of these groups of powder are summarized in Tables 118–120, according to Roth and Capener [1]. Potassium salts are added (Tables 118 and 119) as flash reducing agents. Lead salts (Table 119) are decomposition 'moderators' which play a role in producing low temperature coefficients of burning propellants and a low exponent n in the expression

$$\nu = k\,p^n,$$

where

ν – is the rate of burning
k – a coefficient
p – pressure under which the propellant is burning.

A low exponent n assures a 'plateau' burning, that is, there is little change in the rate ν with pressure (Preckel [39]).

STABILITY OF SMOKELESS POWDER (Vol. III, p. 559)

The stability of smokeless powder remains one of the major problems connected with the storage of propellants containing nitrate esters. It also forms the main subject matter of an International Symposia which has been organized in Sweden by J. Hansson for over ten years [2].

Tranchant [3] points out that three types of stability can be considered:

(a) chemical stability
(b) mechanical stability
(c) ballistic stability

However (b) and (c) depend on the chemical stability. The same author [4] suggested that the term 'Chemical Stability' should be replaced by a more pre-

TABLE 118. Typical single base powder in U.S.A. [1]

	M6	M10	IMR	EC–NACO
Nitrocellulose (13.15%N)	87	98	100	91.4
Ethyl Centralite	–	–	–	3.8
Basic Lead Carbonate	–	–	–	1.0
Volatile (ethanol + dibuthyl ether)	–	–	–	3.8
K_2SO_4	–	1	1 (added)	–
Diphenylamine (DPA)	1 (added)	1	0.7 (added)	–
DNT	10	–	8 (coating*)	–
Dibutyl Phthalate	3	–	–	–

* See Vol. III, p. 627.

TABLE 119. Common double-base solid propellant in U.S.A. [1]

	M2	M5	M8	M21	N5	MDM
Nitrocellulose (13.25%)	77.45	81.95	52.15	53.0	50.0	48.6 (12.6% N)
Nitroglycerine	19.50	15.00	43.00	31.0	34.9	27.0
KNO_3	2.15	2.15	1.25	–	–	–
Ethyl Centralite	0.6	0.6	0.6	2.0	–	1.1
Graphite	0.3	0.3	–	–	–	–
Triacetin	–	–	–	11.0	–	18.7
Lead Salicylate	–	–	–	2.5	–	–
Lead Stearate	–	–	–	0.5	–	4.6
Carbon Black	–	–	–	0.03 (added)	–	–
Diethyl Phthalate	–	–	3.0	–	10.5	–
2-Nitrodiphenylamine	–	–	–	–	2.0	–
Lead Salts*	–	–	–	–	2.4	–
Candelilla Wax	–	–	–	–	0.2	–

* Composition undisclosed.

TABLE 120. Triple-base propellants in U.S.A. [1]

	M15	M17	M31
Nitrocellulose (13.15%)	20.0	22.0	20.0
Nitroglycerine	19.0	21.5	19.0
Nitroguanidine	54.7	54.7	54.7
Ethyl Centralite	6.0	1.5	
Sodium Aluminium Fluoride	0.3	0.3	0.3
Dibutyl Phthalate	–	–	4.5
2-Nitrodiphenylamine	–	–	1.5

TABLE 121. French smokeless powders [38]

Name	Composition		Calorimetric value cal/g	Gas volume cm^3/g	Force f
Poudre B	Nitrocellulose				
épaisse	12.8% N	98	909	925	10 500
	Diphenylamine	2			
Poudre SD	Nitrocellulose				
épaisse	11.7% N	66	762	1012	9 800
	Nitroglycerine	25			
	Centralite	9			
Balistite	Nitrocellulose	58			
CI	12.5% N		1243	833	12 200
	Nitroglycerine	42			
	Centralite (to add)	1			

cise expression 'Measure of chemical evaluation of propellants'. However the term 'Chemical Stability' will be used for short.

The stability of smokeless powder depends on many factors, not only on the purity of the used nitrate esters, or the presence of a stabilizer, but also on the web thickness of powder grains (Vol. III, p. 55).

Currently the stability tests are directed towards the determination of changes of the stabilizers present in the propellant. The most important methods currently used to evaluate the change of the stabilizer are chromatographic methods.

The pioneering work of Schroeder (Vol. III, p. 563) and [5, 6] should be mentioned.

With the progress of chromatography techniques various methods were used, such as thin-layer chromatography (TLC) which started in 1962 by Hansson and Alm [7] followed by other papers [8, 9] including those on high velocity chromatography [10, 11].

Current research on stability and changes of stabilizers are published in volumes of Symposia [2].

Thus thin layer chromatography (TLC) was extensively used by Volk [12]. TLC and liquid chromatography by Ammann and co-workers [13], gas-chromatography (GC), TLC and high pressure chromatography (HPLC) by Ammann [14]. HPLC was in use by Lebert, Stephen and Zeller [15], Brook, Kelso, Neil and MacLeod [16], Lindblom [17], Sopranetti and Reich [18], Volk [19]. Gas chromatography was used by Sopranetti and Reich [20]. To obtain different retention times for derivatives of diphenylamine, they *N*-acylated the products with heptafluorobutyric anhydride and obtained a high resolution.

Microcalorimetry was also tried as a method of determining the beginning of decomposition of propellants [21–26]. It should be recalled that the first experiments on measuring the heat evolved during the decomposition of nitrocellulose powder were carried out by W. Świętosławski, T. Urbański and co-workers [27] (Vol. III, p. 552, 556).

Brook *et al.* [16] summarized the widely-used stability tests in Table 122 (see also Vol. III, p. 558).

TABLE 122. Most common stability tests [16]

Test	Temperature °C	Time of Test	
Abel Heat	65.5	10–30 min	KI starch paper
Methyl Violet	120	40 min	Methyl Violet paper
Dutch	105	72 hrs	Decomposition monitored by weight loss of sample
Surveillance	80	150 hrs	Brown fumes
Small Vessel	100	5 days	Decomposition by weight loss of sample
NATO	65.5	60 days	Loss in stabilizer determined spectroscopically
Woolwich	80	3 weeks	Loss in stabilizer determined by gas–liquid chromatography

In France and U.S.S.R. the stability test of Vieille is widely used. It consists in heating the samples at 110° or 106.5°C in the presence of litmus paper for a minimum of 70 hours (Vol. III, p. 558).

As pointed out in Vol. III quantitative methods such as Bergmann and Junk, pH measurement of heated samples, Taliani (Vol. II, pp. 26–28) are rarely used for control in magazines.

Volk [12] reported the results of his examination of the products of the changes in diphenylamine (DPA) and ethylcentralite during the storage of single and double base propellants respectively at temperatures between 60 and 95°C until the moment that NO_2 appears (a temperature 65.5°C for 60 days has been approved by NATO [3, 16]). According to Volk the nitrogen dioxide was evolved after more than 800 days.

He established the presence of 28 derivatives of DPA as follows:

> 2-nitro-, *N*-nitroso-, *N*,4-dinitroso-, *N*-nitroso-4-nitro-, 3-nitro-, 2,6-dinitro-, 2,4-dinitro-, *N*-nitroso-2,4-dinitro, 2,2-dinitro-, 2,4,6-trinitro-, 2,4′-dinitro-, *N*-nitroso-2-nitro-, *N*-nitroso-4,4′-dinitro-, 4-nitroso-2-nitro-, 4-nitro, 2,2′-4, 4′-tetranitroso-, *N*-nitroso-2,4′-dinitro-, *N*-nitroso-2,2′-dinitro-, 2,2,4-trinitro-, *N*-nitroso-2,2′,4-trinitro-, *N*-nitroso-2,4,4′-trinitro-, 2,4,4′-trinitro-, 2,4,4′,6-tetranitro-, 2,2′,4,4′-tetranitro-, 2,2′,4,4′,6-pentanitro, 4-nitroso-, 4,4′-dinitro-, 2,2′,4,4′,6,6′-hexanitro-diphenylamine, and picric acid.

Similar results were obtained by Brook *et al.* [16].

Ethylcentralite gave 24 products as follows:

Nitro-, 1,3-dinitro-, 1,3,5-trinitro-benzene; ethyl-, 2-nitroethyl-, 4-nitroethyl-, 2,4-dinitroethyl-, 2,4,6-trinitroethyl-, *N*-2,4,6-tetranitroethyl-, *N*-nitroso-ethyl-, *N*-nitroso-2-nitroethyl-, *N*-nitroso-4-nitroethyl-aniline; 2-nitro-, 4-nitro-, 2,4-dinitro-, 4,4-dinitro-2,2,4,4-tetranitro-ethylcentralit; 4-nitro-, 2,4-dinitro-, 2,6-dinitro-phenol and picric acid.

It is important to note which compounds were formed in single and double base powders during long storage at normal storage temperature.

In 1976 Ammann [14] examined nitrocellulose powder manufactured in 1927 and found derivatives of diphenylamine as follows by TLC: 2-nitro, 2,2′-, 2,4-, 4,4′-dinitro-, 2,2′,4-, 2,4,4′-trinitro and tetranitrodiphenylamine. Also trace quantities of *N*-nitroso-4-nitro and *N*-nitroso-4,4′-dinitrodiphenylamine were detected.

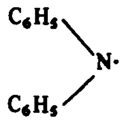
In a 15-year old single base powder Brook *et al.* [16] found 0.77% DPA, 0.23% *N*-nitroso-DPA, 0.02% 2-nitro and 0.04% 4-nitrodiphenylamine. Similar products in much the same quantities were found in nitrocellulose powder subjected to heating at 105°C (Dutch Test) for *ca.* 24 hours and at 65.5°C (NATO Test) for *ca.* 24 days.

FREE RADICALS IN THE CHANGE OF DIPHENYLAMINE

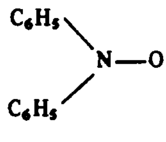
A new and original approach has been given by Mrzewiński [28] to the problem of the change of diphenylamine in single-base powder. He applied ESR technique to follow the transformation of the stabilizer and came to the conclusion that the charge–transfer phenomenon occurs in the first instance at room temperature between nitrocellulose (acceptor) and diphenylamine (donor) in agreement with the finding of T. Urbański *et al.* [29] that nitrate esters give charge–transfer with amines.

The ESR signal was recorded in nitrocellulose powder at room temperature. The intensity of the signal increased at 106.5°C (Vieille test) and reached a maximum after 20 hours.

According to Mrzewiński [30] this was due to the formation of a free radical of diphenylamine (I) a transient free radical of diphenylamine *N*-oxide (II). Free radical I is known to the literature [31]. It yielded *N*-nitrosodiphenylamine (which, as is known possesses stabilizing properties), *N*-nitrosonitro-, dinitro- and higher nitrated diphenylamines. According to Mrzewiński free radical I is



I



II

the active species of the formation of nitroso and nitro derivatives of diphenylamine when single base powder is heated. Short lived free radical II also participated in the formation of nitro compounds, but its role is much less pronounced.

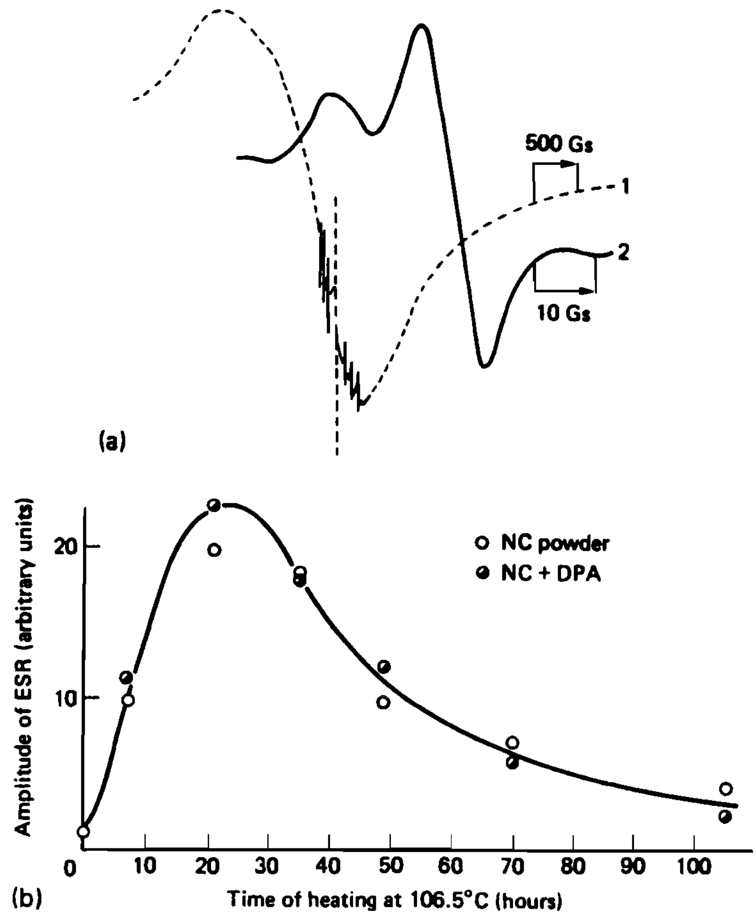


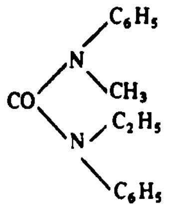
FIG. 109 (a) ESR signal in single-base propellant. 1 – broad line of metal impurities (Mn, Ni, Fe in quantity of *ca.* $10^{-4}\%$), 2 – narrow line of radical species [28, 30]. (b) Intensity of ESR signal against time (hours) of heating single base powder and Nitrocellulose with Diphenylamine at 106.5°C, according to Mrzewiński [28, 30].

STABILIZERS

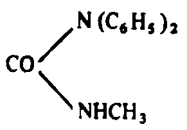
It is well known that diphenylamine (DPA) is too basic as a stabilizer of nitroglycerine and DEGDN (diethylene glycol dinitrate) containing powder. To reduce the basicity of DPA, 2-nitrodiphenylamine (2-NDPA) was introduced into propellants, particularly double base powders, as a successful stabilizer.

A similar action shows *p*-nitro-*N*-methylaniline (*p*NMA).

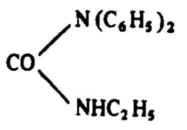
Centralites I and II (Vol. III, p. 645), Centralite III were successful as both stabilizers and 'non-volatile solvents' of nitrocellulose along with urethanes which seem now to be less used. Unsymmetrically substituted urea: unsym-diphenylurea (Vol. III, p. 645) named Acardite I is currently employed as also are its homologues–diphenylmethyl and diphenylethyl urea: Acardite II and Acardite III respectively.



Centralite III
m.p. 60.5°C



Acardite II
m.p. 171°C

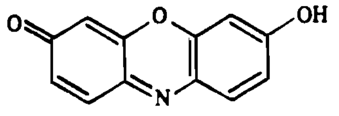


Acardite III
m.p. 73°C

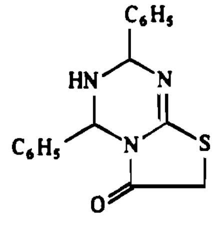
More recently a use has been found for resorcinol as a stabilizer. It readily reacts with nitrogen dioxide to yield nitroso- and nitroresorcinol which can further react with resorcinol molecules yielding various heterocyclics among them resorufin.

The action of this stabilizer was extensively discussed by Blay [32] and Volk [33].

Soliman [42] recently suggested a new stabilizer for double base propellants. This is 5,6,7-trihydro-5,7-diphenyl-thiazolo-[3,2-b]-*s*-triazin-3(2H)-one (III)



Resorufin



III

It gave good results when incorporated, in proportion of 3%, into a double base powder containing, 56% nitrocellulose (12.0% N), 27% nitroglycerine, 9% dinitrotoluene, 4% dibutylphthalate and 1% mineral oil.

When the propellant was kept for 12 days at 100°C, compound III was transformed in mononitro- and dinitrophenyl derivatives of III.

The substance was found to be unsuitable for stabilizing simple base powder due to its insolubility in ether or ether–ethanol.

Volk [33] also described the stabilizing action of a number of compounds. Some lead-salts such as lead salicylate and stearate appear to possess good 'moderating' properties, that is, moderating the decomposition process. As mentioned previously lead salts improve the ballistic properties of propellants lowering the temperature coefficient of burning propellants and helping a 'plateau' burning.

Kinetics of Decomposition

The kinetics of decomposition of single base powder have been studied by Mayet and Lucotte [34]. They found the activation energy $E = 27.5$–36.3 kcal/mol for the temperature range 80–100°C.

The kinetics of decomposition have also been examined by Mrzewiński [28] who rationalized it on the basis of the change of diphenylamine. He came to the conclusion that free radical II does not play a role in the kinetics of the decomposition of powder.

Stability testing of propellants by using microcalorimetry (Vol. III, pp. 552, 556) was recently perfectioned by Elmquist, Lagerkvist and Svensson [50]. It permits measuring the heat effect at 60° or even lower. The instrument consists of four independent calorimeters with a short thermal relaxation time, high sensitivity and excellent baseline stability. In compatibility studies, heat flow curves are recorded for the pure components and a mixture of these. A theoretical curve is constructed, which simulates a non interacting system. The difference between the theoretical and the experimental curve for the mixture reflects the degree of interaction.

Electric Susceptibility of Single Base Powder

Mrzewiński [28] examined the electric susceptibility of a single base powder to detect whether decomposition of nitrocellulose and changes of diphenylamine of ionic character. First the change of dielectric constant with temperature was examined. It showed a trend presented in Fig. 110, typical for dielectric polymers. There is an abrupt increase of the dielectric constant with the increase of temperature around −12°C. The change in the dielectric constant with the age of the powder is given in Fig. 111. A similar trend was observed with laboratory ageing of powder at 106.5°C: there is a slight fall of the dielectric constant with

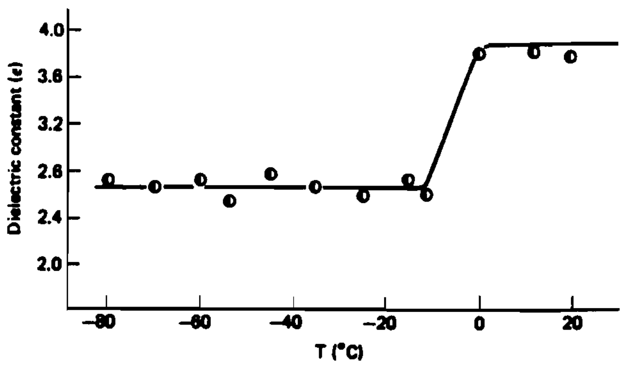


FIG. 110. Dielectric constant of single-base powder against temperature, according to Mrzewiński [28].

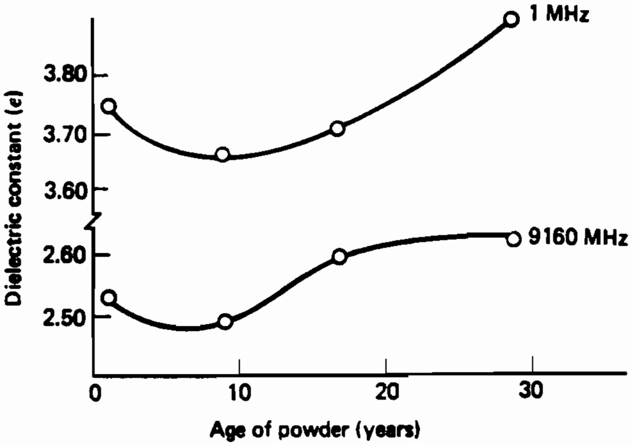


FIG. 111. Change of dielectric constant of single-base powder with the age of powder (Mrzewiński [28]).

a minimum after *ca.* 24 hours of keeping at this temperature. This is probably connected with the change of rational movements of fragments of functional groups.

Erosiveness of Smokeless Powder (Vol. III, 531, 548)

Lowering of the erosiveness of smokeless powder can be achieved by lowering its calorific value. Such is nitroguanidine containing powder (Vol. III, Tables 187, 191). Recently the addition of titanium dioxide and silicon dioxide were suggested as erosion reducing agents [47].

MANUFACTURE OF POWDER

Single Base Powder

Very little can be added to the description in Vol. III, pp. 571–641 and pp. 663–664 on the methods of manufacture of single base propellants.

On the other hand great progress can be seen in the manufacture of double base powder, particularly for rocket propulsion.

Double Base Powder (Vol. III, p. 641)

A few monographic descriptions exist, such as that by Sarner [35], collective volume [36], Encyclopedia [1] and [37], Tavernier [38].

Traditional Double Base Powder

Little can be added to the description of the manufacture of traditional double base powder of the ballistite type (Vol. III, pp. 647–651) where hot rolling is the essential operation for manufacture (Vol. III, Figs 259, 260). Hot rolling is also the central part of the manufacture of solventless powder (Vol. III, p. 654) prior to pressing. Hot rolling in the Kemira factory (Finland) is depicted in Fig. 112.

FIG. 112. Hot rolling of double-base powder in Kemira factory (Courtesy of Kemira OY, Vihtavuori, Finland).

Rocket Double Base Powder

Monographs [36, 37] and Encyclopedia [1] are mainly dedicated to double base rocket propellants. One of the trends of making large 'grains' of rocket propellant charges consists in making charges by casting. The principles of the methods were given in Vol. III, pp. 675–682.

During World War II the Germans used TNT/nitrocellulose cast propellant (Vol. III, p. 681). A similar propellant was developed by T. Urbański [41] in Great Britain during World War II. It was composed of TNT, low viscosity nitrocellulose, potassium nitrate and aluminium.

As previously mentioned (Vol. III, p. 675) two methods of making cast propellants charges are known:

(1) Cast propellant,
(2) Slurry cast propellant.

CAST PROPELLANTS

Some information based on the description by Steinberger and Drechsel [40] is given here. They give the composition of single base, double base and composite cast propellants in Table 123.

TABLE 123. Cast propellants composition [40]

Ingredients	Single Base		Double Base		Composite propellant	
	Casting powder	Finished propellant	Casting powder	Finished propellant	Casting powder	Finished propellant
Nitrocellulose	88	59	75	50.2	30	22.3
Nitroglycerine	–	–	17	44	10	32.8
Plasticizer	5	36				
Lead salts (e.g. lead stearate)*	5	3.4	6	4	–	–
NH_4ClO_4	–	–	–	–	28	20.8
Al	–	–	–	–	29	21.6
Stabilizer	2	1.6	2	1.8	3	2.5

* 'Ballistic Additives'.

Method of Manufacture

Casting powder is composed of small cylinders of *ca.* 1 mm diameter and length. The manufacture of casting powder consists in the operations as follows typical for smokeless powder [40]:

1. Mixing in the presence of solvents (alcohol/ether),
2. Extrusion by cutting the threads,
3. Drying to remove the volatile solvent at 60°C,
4. Finishing by polishing and covering with graphite, screening.

Propellant manufacture from casting powder and solvent consists of the following steps:

1. Filling a mould with casting powder, to occupy *ca.* 68% of the volume,
2. Evacuation by reducing the pressure below 10 mmHg,
3. Casting to fill the interstitial space with casting solvent – a mixture of nitrocellulose and plasticizers (Vol. III, p. 677, Fig. 270).

   The casting solvent may be introduced from the top, from the bottom or radically from perforated cores.

   Some types of casting powder are best cast *in vacuo*, and some under atmospheric pressure.

4. Curing under pressure: the solvent is introduced under pressure *ca.* 4 kg/cm^2 and a pressure of *ca.* 14 kg/cm^2 with a piston is applied on the solid (Fig. 113).

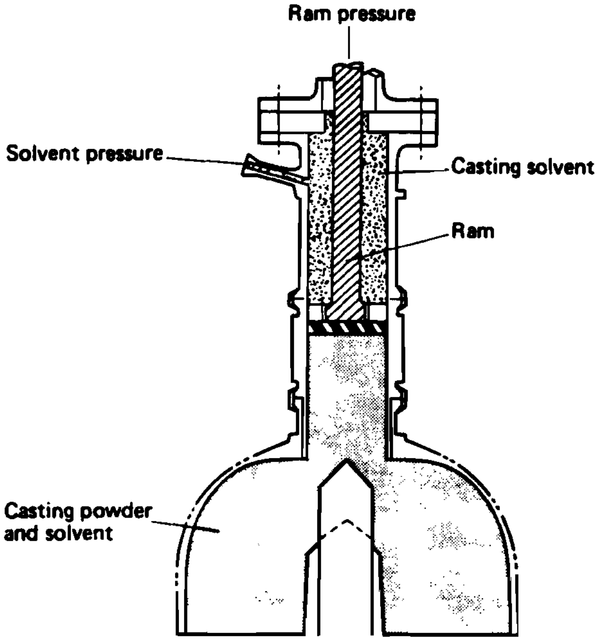


FIG. 113. Casting, curing and applying ram and solvent pressure of double-base rocket propellant [40].

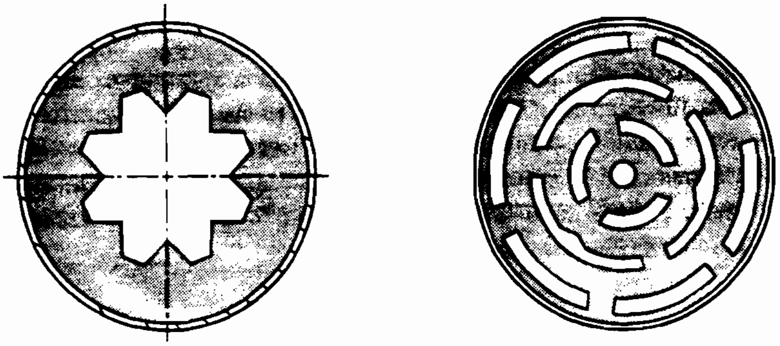
Finished propellant grain has different shapes assuring the best ballistic performance – Fig. 114, according to Steinberger and Drechsel [40]. (See also Fig. 130 in Chapter XXIII).

There is however a problem of the migration of nitroglycerine into the lining which is an inhibitor of combustion. It is usually made of polyesters (Vol. III, p. 677, Fig. 270 and Fig. 115 this volume). Caire-Maurisier and Tranchant [43] examined modifications of the composition of lining and came to the conclusion that by introducing electron accepting groups into the composition of the lining migration could be inhibited. The electron accepting groups would repell the electron acceptor which is nitroglycerine. Practically all polymers were effective in containing chlorine, for example, polymers with units of octochlorodiphenyl. On the migration of nitroglycerine in ballistite propellants – see also Vol. III, p. 651.

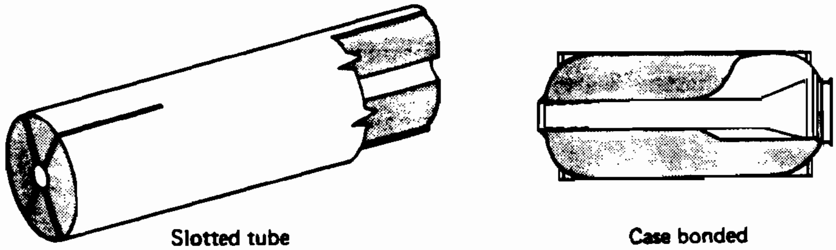
SLURRY-CAST PROPELLANTS (PLASTISOL PROPELLANTS)

(Vol. III, p. 677)

A new description of slurry-cast propellants ('Plastisol Propellants') has been given by Camp [44]. Fine particle spheroidal nitrocellulose is the base of the



Star–perforated Multi–perforated



Slotted tube Case bonded

FIG. 114. Cast grains of rocket propellants. Cellulose acetate inhibitor is shown on the periphery of grains [40].

slurry-cast propellant. Olin Mathieson ball powders of various sizes (Vol. III, pp. 632–639) form a good basis for slurry cast propellants. They have been known and used for this purpose since 1947. A novel method of producing spherical nitrocellulose with an average particle size of *ca*. 10 μ was developed in 1959 by Naval Ordnance research units. The method consists in complete solution of nitrocellulose in nitromethane and dispersion in water with the aid of a colloid mill and an emulsifying agent.

A typical composition of the propellant is as follows [45]:

Spheroidal nitrocellulose (12.2 or 12.6% N)	5–20%
Nitrate esters (nitroglycerine, DEGDN etc.)	25–40%
Desensitizing plasticizers (e.g. dibutyl phthalate)	0–10%
Stabilizers (centralite or 2-nitrodiphenylamine)	0.5–2.0%
Oxidizers (NH_4ClO_4, RDX)	40–50%
Metallic fuel (Al, Be)	0–20%

Mixing is carried out in air-powered or jet in inert liquids or in planetary mixers.

Spheroidal nitrocellulose is first dispersed in a solution of plasticizers and stabilizers followed by adding metal powder (if used) and oxidizers. The temperature of mixing is maintained below 30°C to avoid an excessive gelatinization and an increase of viscosity. After forming the charge it is cured at 40–60°C for a few days. Rubber lining with a cross-linked adhesive system was used to protect the outer surface of the charge.

SCREW-EXTRUSION PROCESS

The worm screw extrusion process (Vol. III, p. 659) is a new and original method for the production of double base powder developed in Germany at Dynamit Nobel A.G. A detailed description appeared recently [46]. The main part of the apparatus is a twin screw extrusion apparatus with two shafts rotating in the same direction – see the monograph by Janssen [46] – Fig. 115.

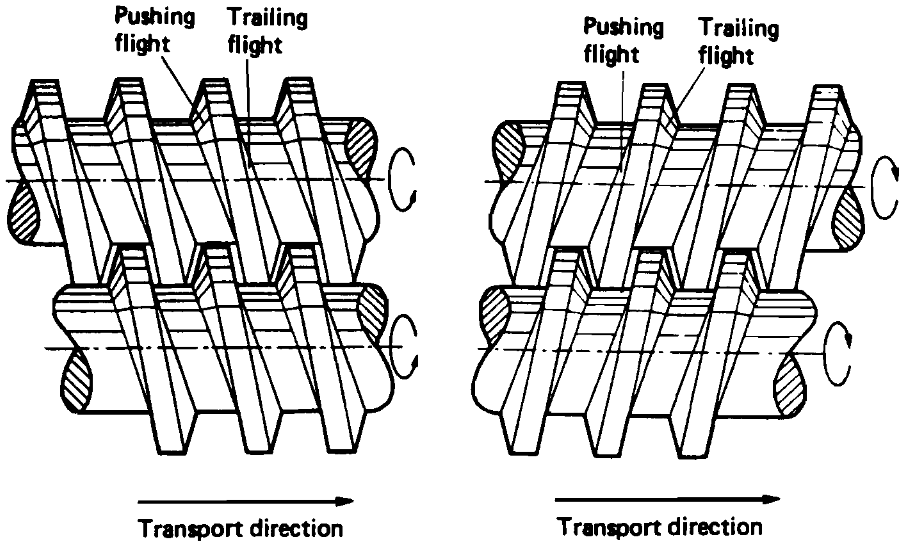


FIG. 115. Twin extrusion, according to Janssen [46].

This is a perfection of the original single screw extrusion apparatus (Vol. III, p. 658, Fig. 266).

The paper by Homburg and Brachert [45] describes the steps as follows:

(1) Mixing of ingredients under water,

(2) Dehydration to 15–20% water and gelatinizing the propellant charge by kneading,

(3) Granulation of the kneaded material for further dehydration and gelatinization in the granulating plant (I),
(4) Blending of the granulate,
(5) Second granulation in granulation plant (II),
(6) Drying the granulate in the drying plant,
(7) Shaping of the pellets into the raw grain, in the extrusion plant.

Kneading is a double-disc screw, that is, an eccentric disc mounted on two shafts rotating in the same direction, the screws are water cooled. Feeding of kneader is continuous. The water is thus separated from the material.

Granulation consists of steps: granulation (I) of lumpy material which returns to the mixing unit and back to granulation and to a twin-screw extruder.

Granulate I passes to the blending unit and then to granulation unit II. The material is dried and shaped in the extrusion plant with a twin-screw extrusion extruder with two shafts rotating in the same direction.

The propellant is plasticized in the twin-screw extruder and the final shape is eventually given.

The propellant is composed of nitrocellulose, nitroglycerine, plasticizer and stabilizers. The method is used to make tubes or cigarette burning cylinders.

The advantage of the described process is in it being continuous, with minimum personnel at a remote control.

Figure 117 shows a roller conveyer of the finished tubular product [45].

Bofors Nobel Chematur [48] have recently described a novel method of making a double-base powder as depicted in Fig. 118. Nitrocellulose, nitroglycerine and additives (e.g. centralite and a solvent) is to pelletize the powder paste, this is done in batches. All the ingredients are charged in the form of a slurry together with a solvent, to a pelletizer (1). The slurry is heated and the solvent makes the nitrocellulose fibres stick together in pellets of about 1 mm size. The heating continues until all the solvent is driven off and recovered. The upper and lower parts of the pelletizer are shown in Figs 119 and 120 respectively. The slurry in the pelletizer is cooled and pumped to a storage tank (2), where the pellets are settled in water. The water in that tank is used for the next pellet batch.

The pelletized material is transported as a water suspension to a screw extruder (3). The extruder drains the pellets, kneads them to a homogeneous material and extrudes through a slotted tube of propellant. The slotted tube is cut into granules (Fig. 121) by a rotating knife and stored under water in another storage tank (4). When enough material has been produced the granulate is agitated to form a uniform mixture and transferred to the second tank (5).

In an extrusion the granulate of the second storage tank is transformed into the finishing propellant by the same type of extruder as in the first extrusion step. The propellant tubes, single or multiperforated are extruded through the dies (60 directly into flowing water which transports them to a cutter. They are

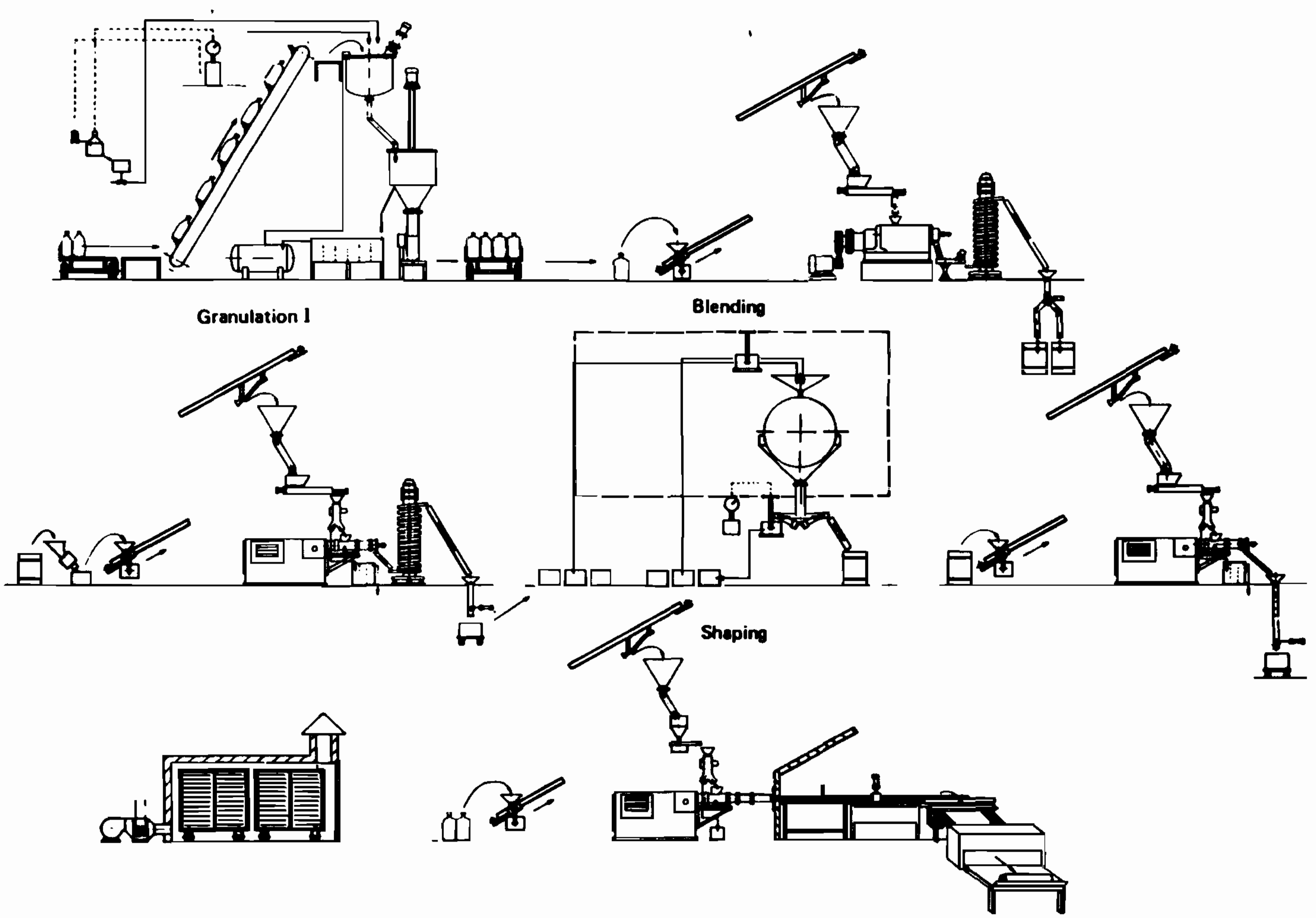


FIG. 116. Twin extrusion process of manufacturing double-base rocket propellants, according to Homburg and Brachert [45].

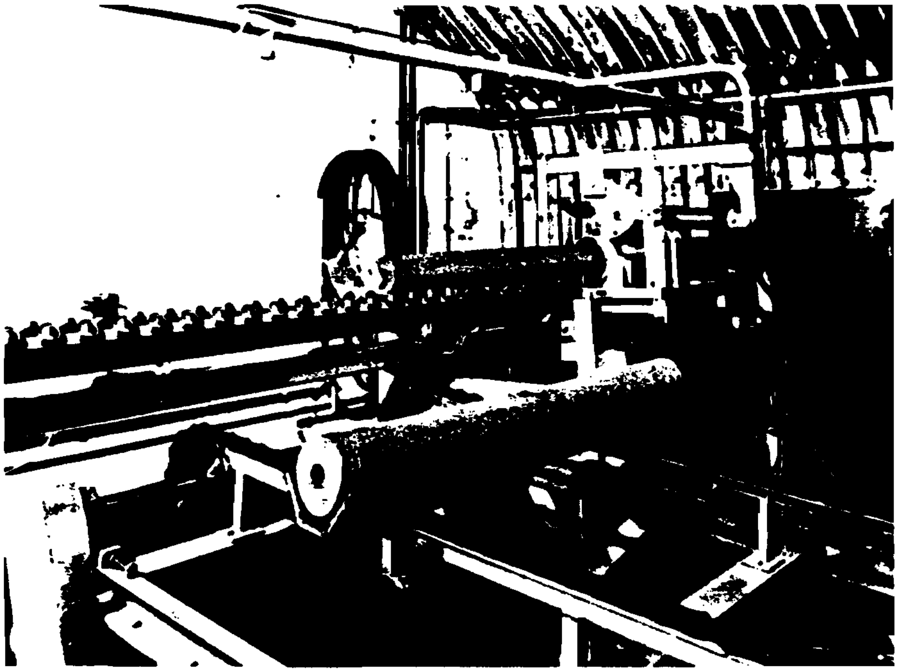


FIG. 117. Roller conveyer of finished tubular product Courtesy Dynamit Nobel A.G., D-5000 Köln (Dellbrück).

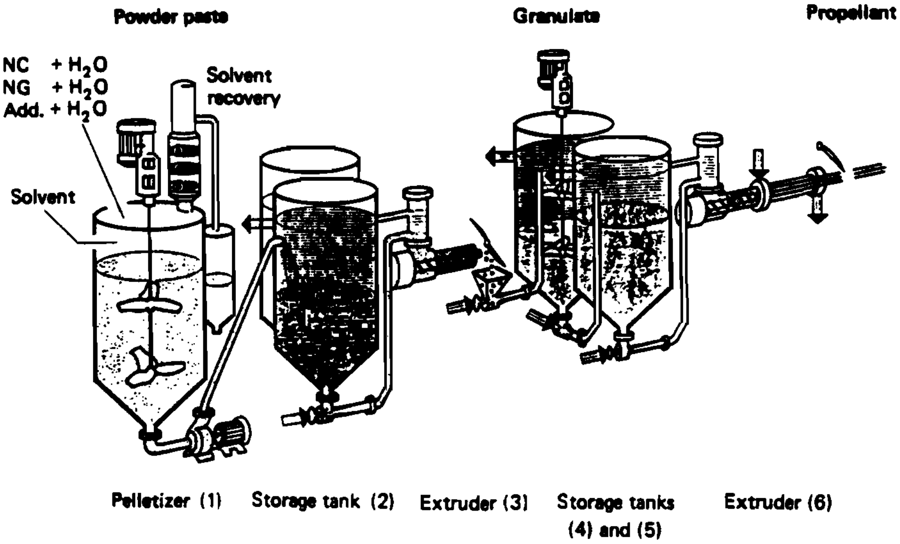


FIG. 118. Novel method of making a double-base powder of Bofors Nobel Chematur.

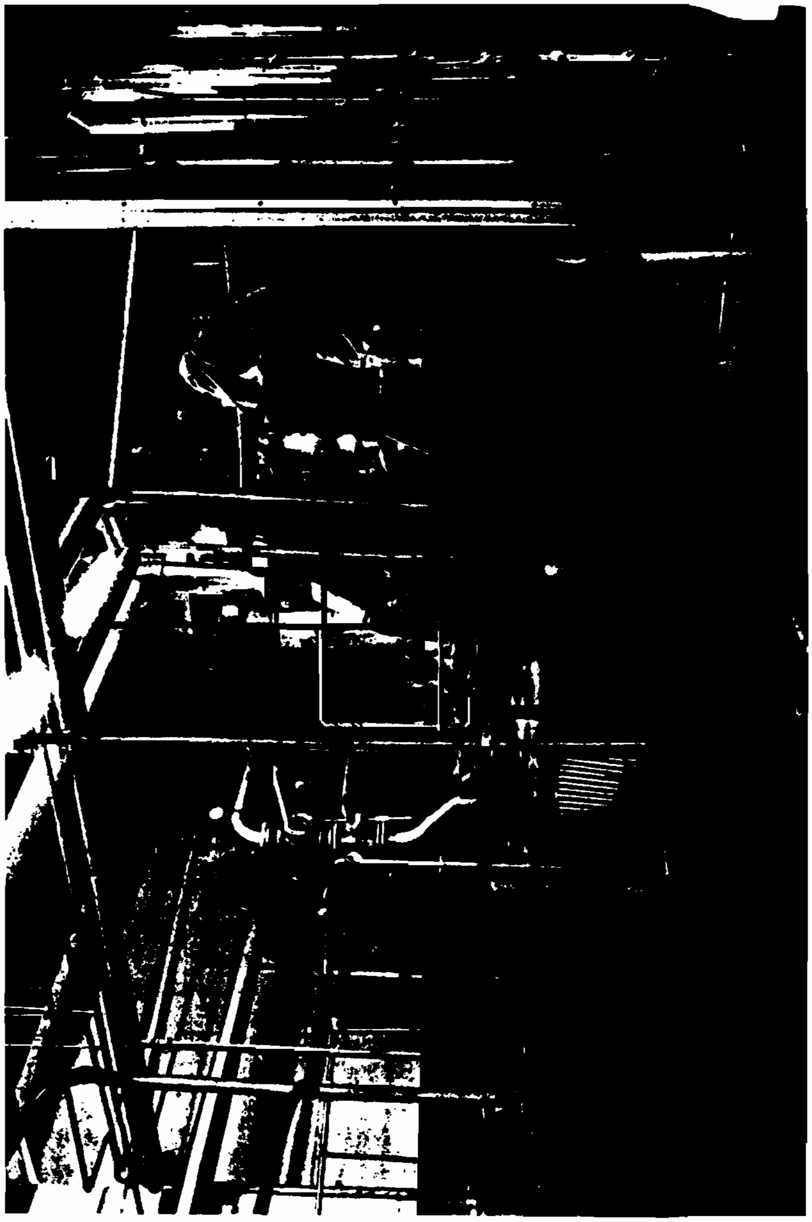


FIG. 119. Pelletizer of a double-base powder, upper part (courtesy Bofors Nobel Chematur).

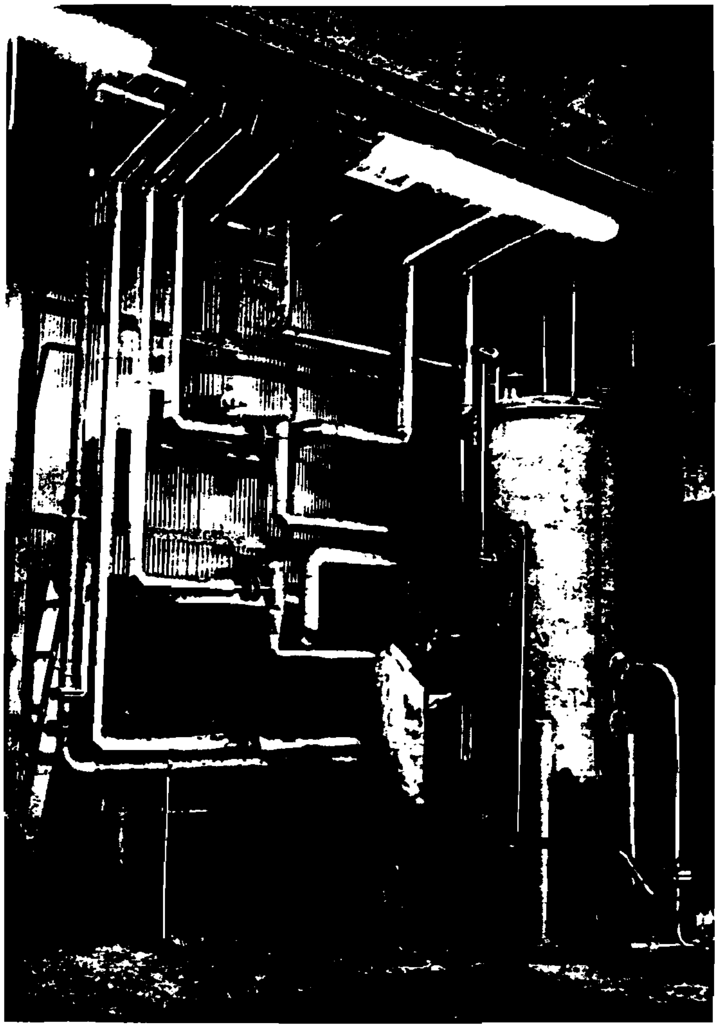


FIG. 120. Pelletizer of a double-base powder lower part (courtesy Bofors Nobel Chematur).

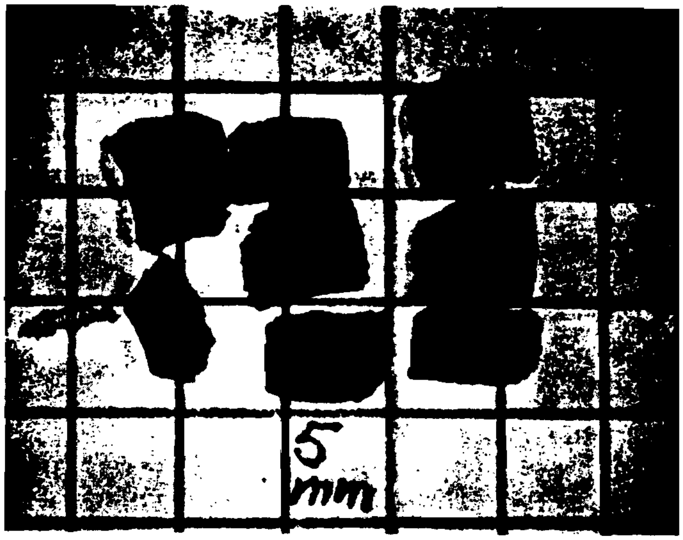


FIG. 121. Granules of a double base powder (courtesy Bofors Nobel Chematur).

cooled by water which reduces the evaporation of nitroglycerine from the cut propellants.

The propellant with a low water content constitutes a risk of explosion if ignited. For that reason the extruders are placed in a separate room. Figure 122 gives a view from inside the room for final extrusion and Fig. 123 – the cutters. The mean production is 50 kg/hr per extruder.

The factory of Bofors has experienced a few explosions caused by ignition in the extruders. The ignition was by a foreign object produced in the extruded material. The remote control operation gives a higher safety level. This new method reduces the manual work and the exposure to nitroglycerine and increases the safety of the manufacture.

Classical Extrusion Method

The modernized classical extrusion method of double base powder by means of a heated hydraulic press Werner and Pfleiderer is shown in Fig. 124.

HIGHER ENERGY SMOKELESS PROPELLANTS (Vol. III, p. 670)

The attempts to increase the energy of smokeless powder by adding a considerable amount of PETN did not pass beyond large-scale experiments. Also the use of polymers containing nitro groups (Chapter XIV) does not seem to have a practical application for propellants.

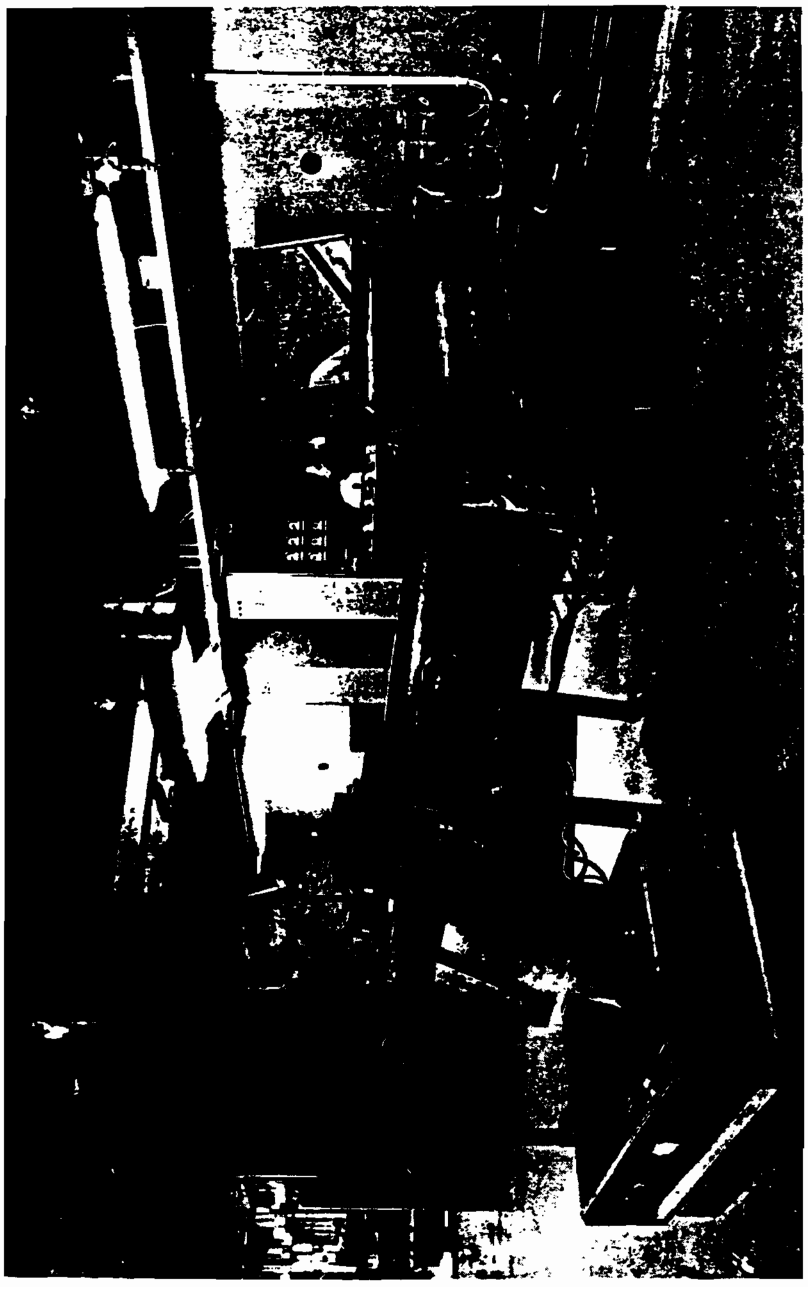


FIG. 122. The room for final extrusion of a double base powder (courtesy Bofors Nobel Chematur).

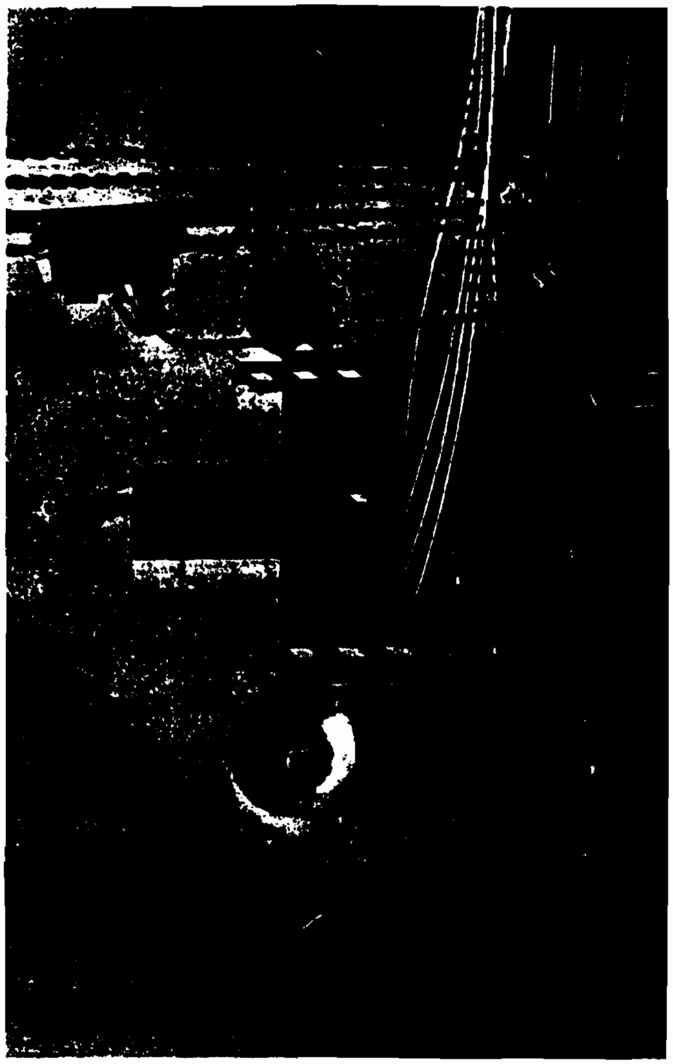


FIG. 123. The cutters of a double base powder (courtesy Bofors Nobel Chematur).

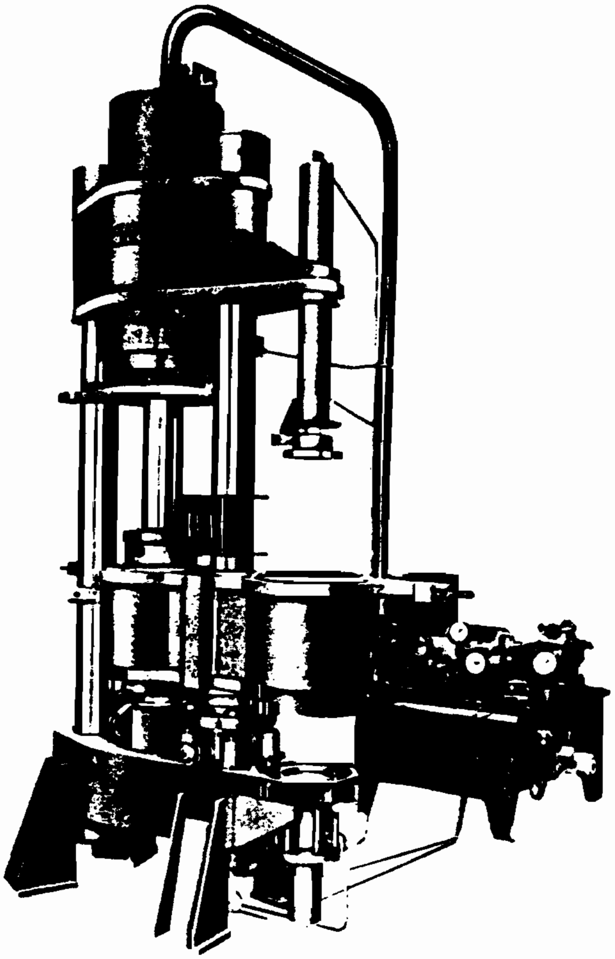


FIG. 124. Modernized classical heated extrusion press for double-base powder (Courtesy Werner & Pfleiderer, D-7000 Stuttgart, FRG).

Nevertheless there are continuing attempts to introduce such compounds as RDX and HMX into smokeless powder. Thus Sumi and Kubota [49] described double base powder containing up to 27% HMX. The propellant was characterised by a low exponent n even at low pressure: $n = 0.3$ at 20 atm.

The addition of RDX or HMX into composite propellants is also known – see Chapter XXIII.

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CHAPTER 23

COMPOSITE PROPELLANTS

(Vol. III, p. 365)

INTRODUCTION

Roth and Capener [1] formulate composite propellants as follows:

'Composite propellants which are used almost entirely in rocket propulsion normally contain a solid phase oxidizer combined with a polymeric fuel binder with a $-CH_2-CH_2$-structure. Practically speaking ammonium perchlorate is the only oxidizer which has achieved high volume production, although ammonium nitrate (AN) has limited special uses such as in gas generators. Other oxidizers which have been studied more or less as curiosities include hydrazinium nitrate, nitronium perchlorate, lithium perchlorate, lithium nitrate, potassium perchlorate and others. Among binders, the most used are: polyurethanes, polybutadiene/acrylonitrile/acrylic acid termopolymers and hydroxy-terminated polybutadienes.'

According to recent information [2], the space shuttle's orbiter *Columbia* was powered by two solid rocket motors with a propellant which consists of:

ca. 70% Ammonium Perchlorate (AP),
16% Al powder,
12% polybutadiene–acrylic acid–acrylonitrile (PBAN) termopolymer (a combustible binder),
2% liquid epoxy resin (a curing agent), and in addition
0.17% iron oxide powder (as a catalyst).

Each rocket motor is loaded with more than one million pounds (*ca*. 454,000 kg) of solid propellants.

The problems of Composite Propellants is a fast developing branch of propellants chemistry and technology. The following are monographs (in addition to those mentioned in Vol. III) dedicated to composite propellants: [3–8, 27]. The Encyclopedia of Kaye [1] and collective volume [6] are particularly important sources of information.

A vast amount of work is being done and continuing progress now merits a special modern monograph. Only the principles of the formulation of composite propellants and their manufacture will be given here. The description will be based on different polymeric binders mainly with ammonium perchlorate. Some data on the thermal decomposition of ammonium perchlorate will be given here to complete the information in Chapter XVI.

An important feature of ammonium perchlorate propellants is their decomposition at high temperature. Differential thermal analysis of NH_4ClO_4 is given in Fig. 125, according to Sarner [4]. It can be seen that appreciable decomposition occurs at temperatures lower than the main exotherm.

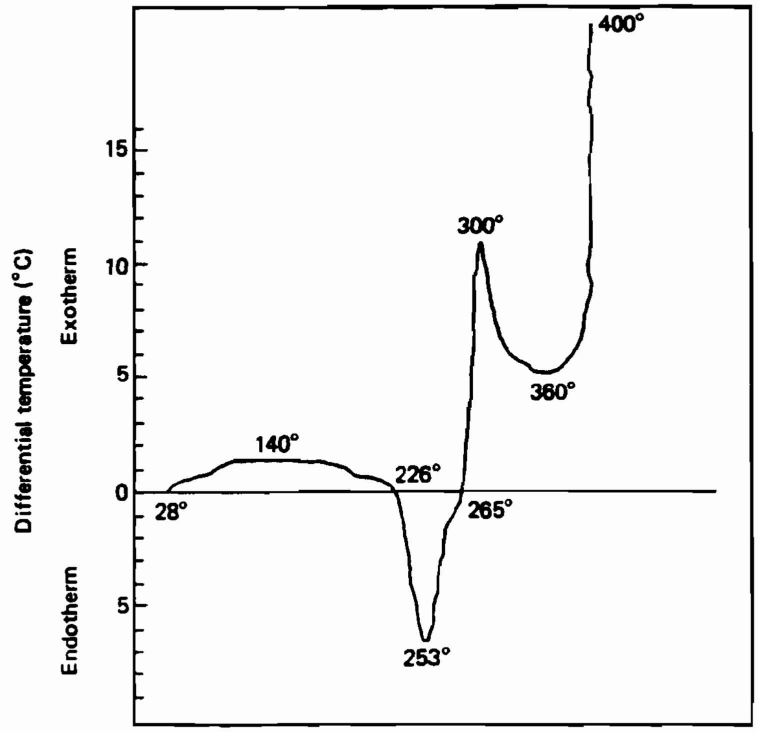


FIG. 125. Differential thermal analysis of NH_4ClO_4 from Propellant Chemistry by Stanley Sarner [4]. Copyright © 1966 by Van Nostrand Reinhold Company. Reprinted by permission of the publisher.

The ammonium perchlorate crystal size is of great importance.

Baldwin and Reed [24] give figures for the rate of burning of ammonium perchlorate composite propellant depending on the size of crystals of the salt as:

Particle size of NH_4ClO_4	Rate of burning cm/sec
75 μ	5.1
35 μ	6.1
15 μ	7.6
5 μ	9.2

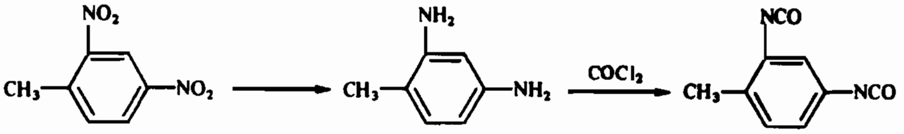
POLYURETHANE BINDERS

As is known, urethanes are formed by reacting isocyanates with hydroxyl carrying compounds:

$$\mathrm{RNCO + R'OH \longrightarrow R\,NHCOOR'}. \qquad (1)$$

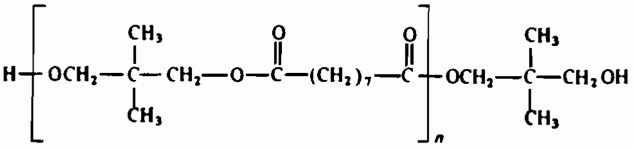
With di- or polyfunctional isocyanates and dihydroxylic compounds a rubbery polymer is obtained and with tri-hydroxylic alcohols cross-linked polymers are formed.

The most common polyurethane binders are from 2,4-toluene diisocyanate (TDI) obtained from 2,4-dinitrotoluene by the sequence of reactions (2):



(2)

and long chain glycols with primary and secondary alcoholic groups. According to Oberth and Bruenner [9] among the glycols are those with: (a) an ester function, e.g. I:



$$\mathrm{H}\left[\mathrm{OCH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}}\right]_n\mathrm{OCH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2OH}$$

I

(b) and ether function as poly (1,2-oxypropylene)diol (PPG) of $M = ca.\ 2000$.
(c) polybutadiene chain.

Binder (b) and (c) are more advantageous than (a).

Binders (b) are more readily available, show a low viscosity, good rate of cure and good ageing stability. Their disadvantage is ease of absorbing oxygen to form peroxides, but the addition of aromatic amine antioxidants removes this disadvantage. They withstand prolonged storage (several years) at temperatures of 65–82°C without the loss of mechanical properties.

Hydroxyl-terminated polybutadienes (c) are readily subjected to air-oxidation and subsequent hardening.

Polyfunctional alcohols, mainly trifunctional and their esters are used as cross-linking agents.

Table 124 gives typical compositions of unaluminized polyurethane resin propellants, according to [10].

TABLE 124. Polyurethane resin propellants JPL X500

Components	Wt% 70%	80% Oxidizer
NH_4ClO_4		
ground*)	21.0	24.0
unground*)	49.0	56.0
Polypropylene glycol	23.9	15.9
Toluene Diisocyate (TDI)	4.8	3.2
1,2,6-Hexanetriol (HT)	1.2	0.8
Ferric acetyl acetonate	0.1	0.1

* A bimodal oxidizer system is used, consisting of 30% ground and 70% unground ammonium perchlorate.

The propellant shows good mechanical properties (tensile strength, elongation and initial modulus) at temperatures from –40° to +70°C.

By the addition of aluminium (and berillium) higher energy propellants are formed. Figure 126 gives, according to Oberth and Bruenner [9], the calculated specific impulse of ammonium perchlorate–aluminium–polyurethane (polyether) binder (max. I_s = 247 s).

POLYBUTADIENE BINDERS WITH CARBOXYLIC FUNCTION

The polybutadiene polymers containing carboxyl functional groups appear to be the most important group of binders in composite propellants. The following are co-polymers used in this type of propellant, according to Mastrolia and Klager [11]:

(1) butadiene and acrylic acid (PBAA),
(2) terpolymer of butadiene, acrylic acid and acrylonitrile (PBAN),
(3) the carboxyl terminate polybutadiene (CTPB).

Here is a brief description from the same source [11].

(1) PBAA was the first butadiene polymer to be used in rockets. It was made by free radical emulsion polymerization to an average M = 3000. It was a random mixture of polymers of different molecular weights and functionality

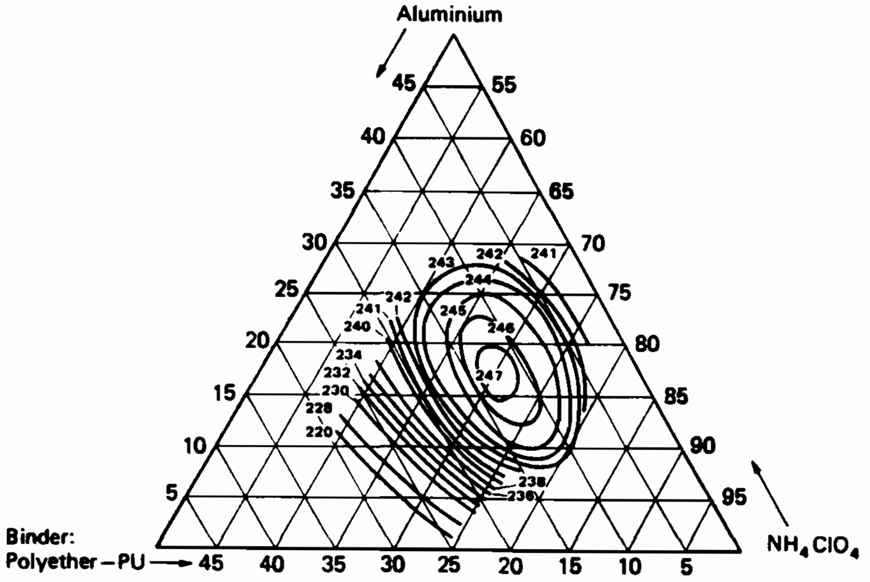


FIG. 126. Calculated Specific Impulse of ammonium perchlorate–aluminium–polyurethane (polyether) binder, according to Oberth and Bruenner [9].

and therefore did not possess proper mechanical properties. The use of such polymers was eventually discontinued.

(2) PBAN was also made by emulsion polymerization. Mechanical properties of polymer were improved through steric action by introducing acrylonitrile. Also acrylonitrile reduced deteriorating action of oxygen on double bonds of the polymer as known to be suppressed in nitrile rubber.

The following are data for the physical properties of PBAN:

Molecular weight	3000–4500
Viscosity at 25°C	300–350 poise
Density	0.93–0.94.

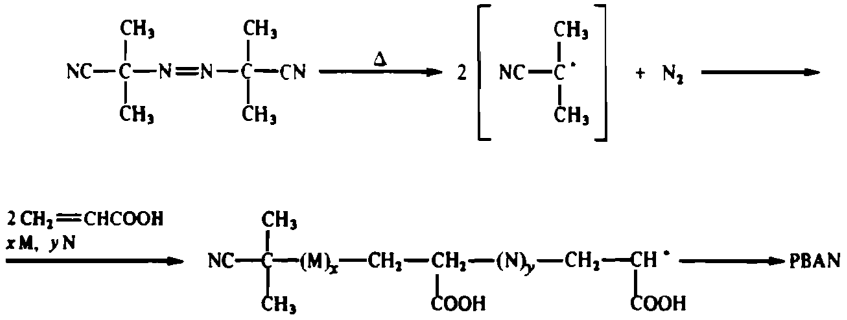
The composition of propellants with PBAN and of increased energy through the addition of Al is kept within the limits in wt. %:

$NHClO_4$	60–84
PBAN	12–16
Al	2–20
Stabilizer	0–1
Curing agents	0.2–1.0

The resistance against the action of oxygen can be seen from the effect of keeping the propellant in oxygen atmosphere at 105°C at 96 hours:

	Hardness	
	internal	surface
Before the action	40	40
After 96 hours	49	47

The PBAN preparation can be presented by scheme (3). The butadiene–acrylic acid–acrylonitrile can be varied over a wide range.



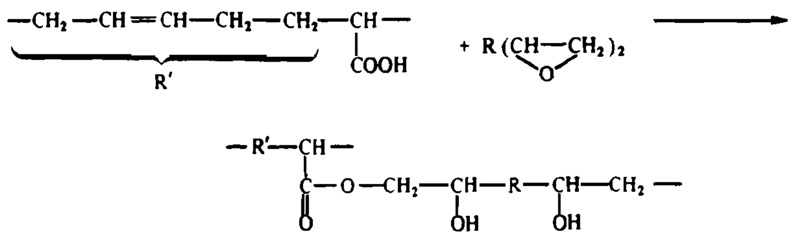
(3)

$M = CH_2—CH—CH = CH_2$

$N = CH_2 = CH—CN$

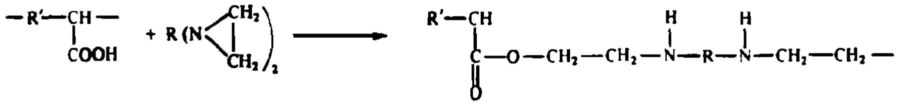
The acrylic acid and acrylonitrile are fed into the reactor containing the butadiene emulsion and the chain termination is achieved by adding a mercaptan when the molecular weight reaches 2000–4000. After that an antioxidant is added, the polymer purified by washing with water and vacuum drying.

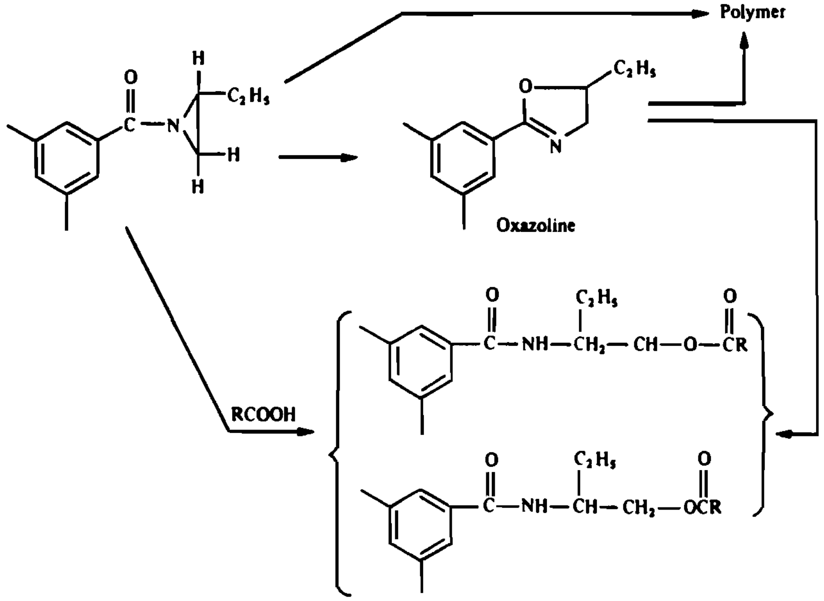
To form a three-dimensional structure the curing reaction is carried out through difunctional epoxides (4) or aziridines (5), *R* is curing agent radical e.g. (6). Carboxylic groups supply *N*-hydrogen atoms. The PBAN polymer has a sufficient number of functional group to produce a firm gel without using separate cross-linking agents



(4)

(5)

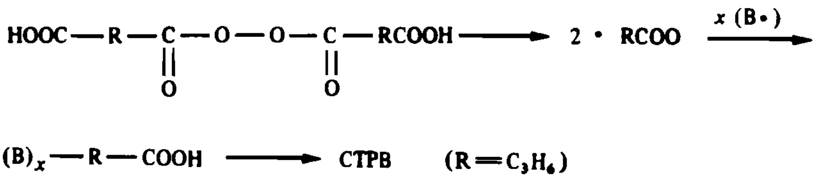




(6)

(3) CTPB – Carboxy Terminated Polybutadiene free radical terminated polymers.

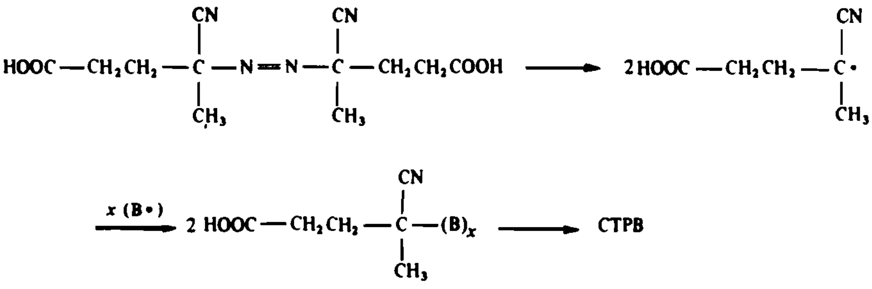
Two methods have been given by Mastrolia and Klager [11]. One of the methods is by using the glutaric acid peroxide as the initiator of free radical and butadiene (7):



$$HOOC-R-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-RCOOH \longrightarrow 2\cdot RCOO \xrightarrow{x\,(B\cdot)}$$

$$\cdot(B)_x-R-COOH \longrightarrow CTPB \quad (R{=}C_3H_6) \qquad (7)$$

Another method used 4,4′-azobis-4-cyanopentanoic acid as the initiator:



$$HOOC-CH_2CH_2-\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}-N{=}N-\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2COOH \longrightarrow 2HOOC-CH_2CH_2-\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot + N_2$$

$$\xrightarrow{x\,(B\cdot)} 2\,HOOC-CH_2CH_2-\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}-(B)_x \longrightarrow CTPB \qquad (8)$$

Here is an example of the composition of a CTPB propellant according to [28]:

Ammonium perchlorate	80.0–80.9%
Al powder	5.
CTPB	14
Ferric oxide	0.1–1.0

HYDROXYTERMINATED POLYBUTADIENE BINDER (HTPB)

An example of a composite propellant with hydroxyterminated polybutadiene binder is given here [28]:

Ammonium perchlorate	77.6–76.0%
Al powder	10
HTPB	11.6
Ferric oxide	0.4–2.0

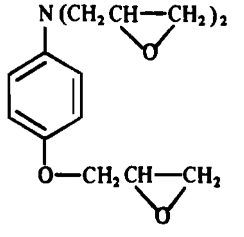
CURING BUTADIENE POLYMERS

Carboxyl terminated polybutadiene polymers require curing in order to form a tridimensional network. Polyfunctional epoxides and aziridines are used for cross-linking.

When making propellants with ammonium perchlorate the oxidizing properties of the latter produce side reactions interfering with the action of the curing agent. This involves the formation of a less complete three dimensional structure.

The structure of a few epoxide and aziridine curing agents are given (II–VIII).

Epoxy compound IV exhibits a minimum of side reactions in the presence of ammonium perchlorate. Epoxy curing agent II shows a high reaction rate but side reactions dominate in the presence of ammonium perchlorate. The compound BITA (V) can be subjected to various transformations shown in scheme (6). They also possess similar properties as V but are less active. Zirconium



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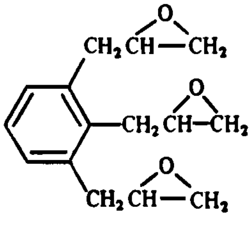
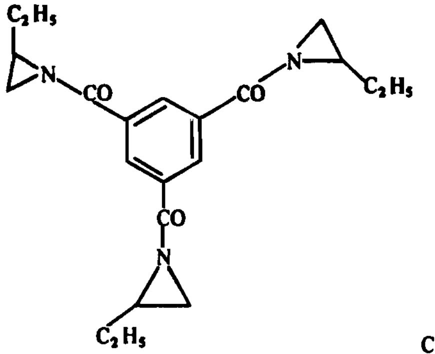
II

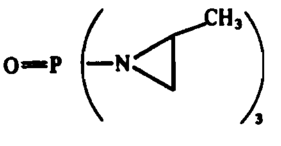


Epon X-801

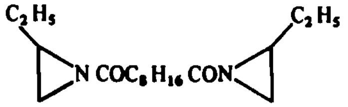
III



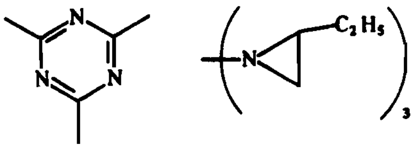
BITA
V



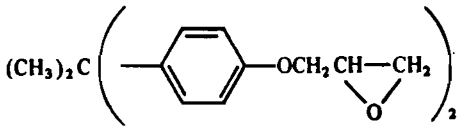
MAPO
VII



BISA
VI



TEAT
VIII



DER-332
IV

acetylacetonate is an effective polymerization catalyst and can be added in quantity 0.5 wt. %. Propellants made with MAPO (VII) possess good properties but a problem arises with ageing, probably due to the presence of P–N bond. A mixed curing agent made of VII and II gave more satisfactory results.

The fact that a variety of reactions given by different curing agents led to developing mixed curing agents composed of both epoxy- and aziridine compounds. This is still a developing side of problems of composite propellants – a specialized problem – connected with polymer chemistry and technology and outside the scope of the present book.

Figure 127 gives theoretical specific impulse for ammonium perchlorate-Al-polybudiene propellants. The maximum specific impulse was calculated as high as I_s = 266s [11].

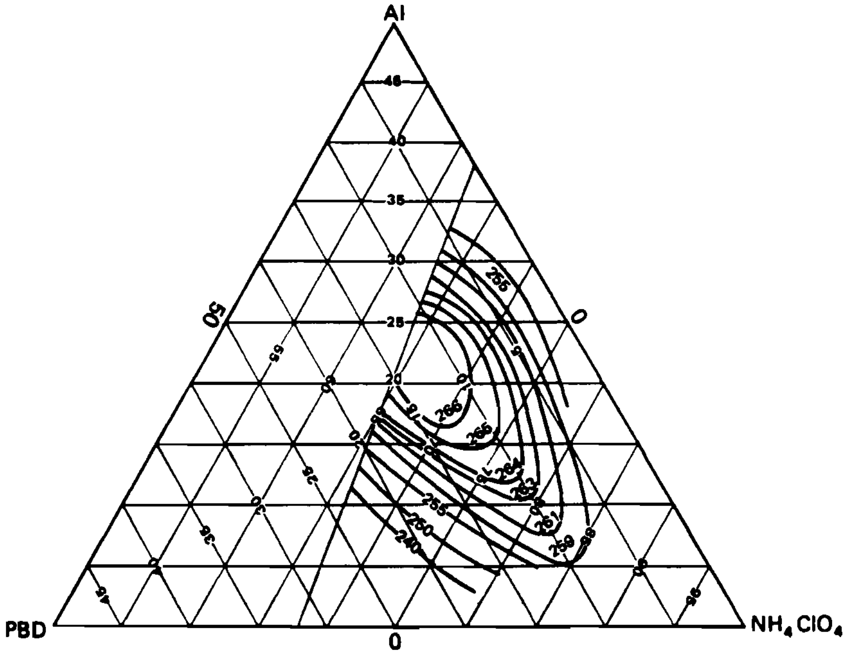


FIG. 127. Calculated specific impulse of ammonium perchlorate–aluminium–polybutadiene (PBAN) according to Mastrolia and Klager [11].

POLY (VINYL CHLORIDE) PLASTISOL PROPELLANT (PVC)

According to the description by Rumbel [12] PVC plastisol propellant consists of ammonium perchlorate, uniformly dispersed and cured PVC plastisol. A number of propellants have been developed by the Atlantic Research Corporation under the name Arcite.

Standard Arcite has the composition in wt. %.

NH_4ClO_4 (equal parts of coarser and finer passing through mesh 62 μ)	75.0
PVC	12.5
Plasticizer (dibutyl sebacate)	12.5
Stabilizer (undisclosed compound) added	0.4

The influence of adding aluminium (or magnesium) to increase the specific impulse I_s up to 242 s is given in Fig. 128. One of the aluminized propellants Arcite 373 D has the composition in wt. %.

NH_4ClO_4	58.9
Al	21.1

PVC	8.6
Plasticizer (2-ethylhexyl adipate)	10.8
Wetting agent (a mixed detergent: glycerol pentaerythritol dioleate, dioetyl sodium sulphosuccinate)	0.25
Stabilizer (undisclosed)	0.35

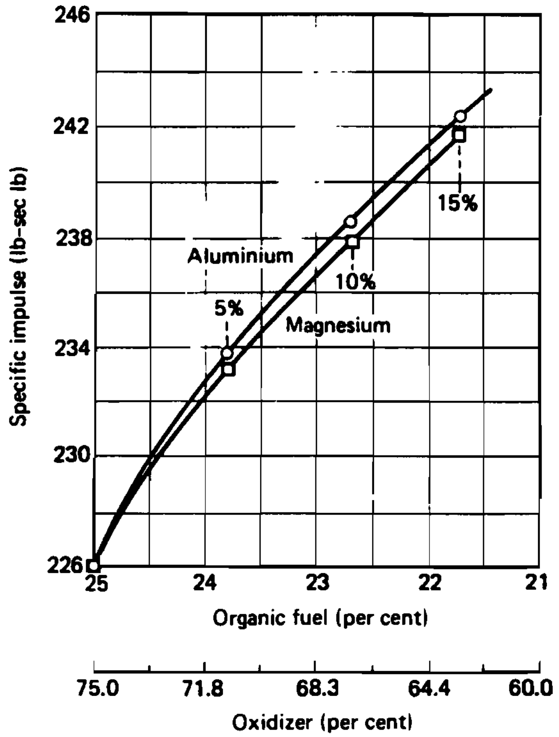


FIG. 128. Increase of specific impulse of PVC Plastisol Propellants by adding Al and Mg according to Rumbel *et al.* in [12].

A stabilizer is added to retard the decomposition of PVC during curing, which is carried out at 150–175°C. Because of low thermal conductivity, several hours are required to raise the central portion of the propellant grain to curing temperature. The portions of the grain close to the source of heating may show a tendency to decompose and stabilizers are added to inhibit the decomposition. It is advisable that the stabilizer should be able to bind the hydrogen chloride which would decompose the polymer. However propellants with aluminium powder show better thermal conductivity and hence the time of cure can be reduced.

This is of course related to all composite propellants with aluminium.

HIGH ENERGY COMPOSITE PROPELLANTS WITH HMX (OCTOGENE)

Attempts have been made to introduce HMX into composite propellants. According to Sayles [13] propellant 'D' is composed of:

Ammonium perchlorate	19.2 wt. %
Butanetriol trinitrate	25.7
HMX	48.5
Ethyl acrylate-acrylic and co-polymer (EA/AA, 95/5)	4.6
Diepoxydicyclohexyl carboxylate (curing agent)	1.5
Carbon black	0.5

Specific impulse $I_s = 262.4$

RDX can be substituted for HMX.

Some other composite propellants were suggested with nitrogen difluoride groups, for example 1,2,3-tris[1,2-bis(difluoroamino)-ethoxy propane] but high cost of the compound did not seem to encourage its use [1].

ROLE OF INGREDIENTS ON PROPERTIES OF COMPOSITE PROPELLANTS

This problem is discussed in detail by Fluke [14] and here is a brief description of his paper.

Ammonium perchlorate of various fineness is used to give a better 'packing'. Particle size distribution is of great importance to density, rheological properties of the viscous mass, mechanical properties and burning of the propellant. Rheological properties obviously depend on polymer binder which is of course the combustible ingredient in propellants.

Here are some of the outlines given by Fluke on this particular matter:

(1) Formula optimization. In the formulation of new propellants, it may be desirable to optimize certain rheological characteristics.

(2) Formulation characterization. Prior to using a new propellant formulation, the material should be fully characterized and analyzed rheologically. Processability predictions may be extrapolated.

In quality control it is necessary to check rheological properties of propellant samples.

In addition to the above, the following are remarks on some components of composite propellants according to the existing literature.

Plasticizers have a very important effect on physical properties of the cured propellants and on the variation of these properties with temperature. Long chain aliphatic plasticizers improve low temperature flexibility. An increase in plasticizer viscosity obviously leads to an increase in viscosity of the mixed propellants. The burning rate is little changed by changing plasticizers.

Attention should be paid to preventing the formation of cracks and voids during cure [15], which are caused by shrinkage during solidification of the propellant. Specific processing conditions are required for each propellant formulation and rocket size according to Arendale [15].

Wetting agents in propellant compositions facilitate mixing ingredients and reduce the viscosity so that they are cast more readily.

Metals

Aluminium should be used in spheroidal shaped particles [12]. It gives a better pourability of the compositions [16].

A very important observation was recently made by Rumbel [12]. This is the incorporation of fine metal wires into a propellant, which increase the rate of burning as recorded originally in PVC plastisol propellants [12] but seems to be now a general practice in composite propellants. Metal wires are introduced into the composition before cure. When the propellant is burned the wires extend from the unburned propellants into the flame zone. They provide paths for rapid heat transfer and thus burning along the wire is faster than outside the wire. Particularly efficient are silver and copper wire, as described by Rumbel – for PVC plastisol propellants (Table 125).

TABLE 125. Burning rates along 5-mm wires in PVC propellants according to Rumbel *et al.* [12]

Wire	Burning rate along wire cm/s	Ratio of burning rate along the wire standard	Properties of metal melting temperature °C
Silver	6.76	5.3	960
Copper	5.92	4.6	1083
Aluminium	2.96	2.3	660
Magnesium	2.45	1.9	651
Steel	2.04	1.6	*ca.* 1460

Also aluminium staple was suggested [17] together with aluminium powder in composite propellant containing MAPO (VII) curing agent.

Catalysts (Vol. III, pp. 369, 394)

The role of catalysts on burning ammonium perchlorate and other salts, such as ammonium nitrate, potassium perchlorate etc. is widely described in the monograph by Glazkova [18].

Cohen Nir [19] described the catalytic action of Cu_2O and powdered metals – Al, B, Mg – on steady burning of ammonium perchlorate under low pressure:

The catalytic action of iron oxides (mainly ferrous oxide) was described by Bakhman and co-workers [20]. They also reviewed the literature on the catalytic action of Fe, Fe_2O_3, Fe_3O_4, organo-iron compounds, Co_2O_3, NiO, Cu, Cu_2O, CuO, Cu chromite, Cu chlorides, Cr_2O_3, salts of chromic acid, MnO_2, $KMnO_4$, V_2O_5, SiO_2, TiO_2.

Iron oxide catalyst mentioned in the description of the space shuttle's orbiter *Columbia* [2] was probably ferric oxide or a mixture of various iron oxides.

BURNING COMPOSITE PROPELLANTS CONTAINING AMMONIUM PERCHLORATE

It has been shown that perchloric acid is liberated from the solid fuel and reacted further. Gilbert and Jacobs [21] found that the major products of decomposition of perchloric acid are oxygen and chlorine which further react with organic compounds to yield CO, HCl, H_2 and chlorinated short chain hydrocarbons. The mechanism of burning comprises the depolymerization of the organic solid phase to give gaseous fuel fragments which react further [22].

Steinz and Summerfield [23] reviewed existing theories on burning ammonium perchlorate under pressure between one and 100 atm. and built a schematic presentation of the mechanism. In the first stage the dissociation occurs of NH_4ClO_4 into NH_3 and $HClO_4$ (A/PA) and reacted with oxidant/fuel (O/F) zone.

The pressure exponent n around 100 atm for ammonium perchlorate propellants is *ca*. 0.3.

Pepekin, Apin and co-workers [28] attempted to rationalize the rate of burning of composite propellants with ammonium perchlorate as a function of the combustible ingredient. They came to the important conclusion that the rate of burning did not depend on the heat of burning, but on the strength of the chemical bond in the combustible substance. A striking example was given by a system with ferrocene. On the basis of the enthalpy of the bond C–Fe (which is 75.0 kcal/mol) it should be expected that the burning rate would be similar to that of ammonium perchlorate with amines. The latter have the enthalpy of the bond C–N equal to 73 kcal/mol. However experiments show that the rate of burning of mixtures of ammonium perchlorate with ferrocene are nearly three times higher than that of ammonium perchlorate with amines.

The authors found an empirical equation:

$$u = 0.9 - 0.005\ E \text{ cm/s},$$

where

u – the rate of burning of the mixture,
E – the energy of the weakest bond of the combustible material.

The bond C — Fe in ferrocene is very weak and ferrocene readily dissociates according to the equation:

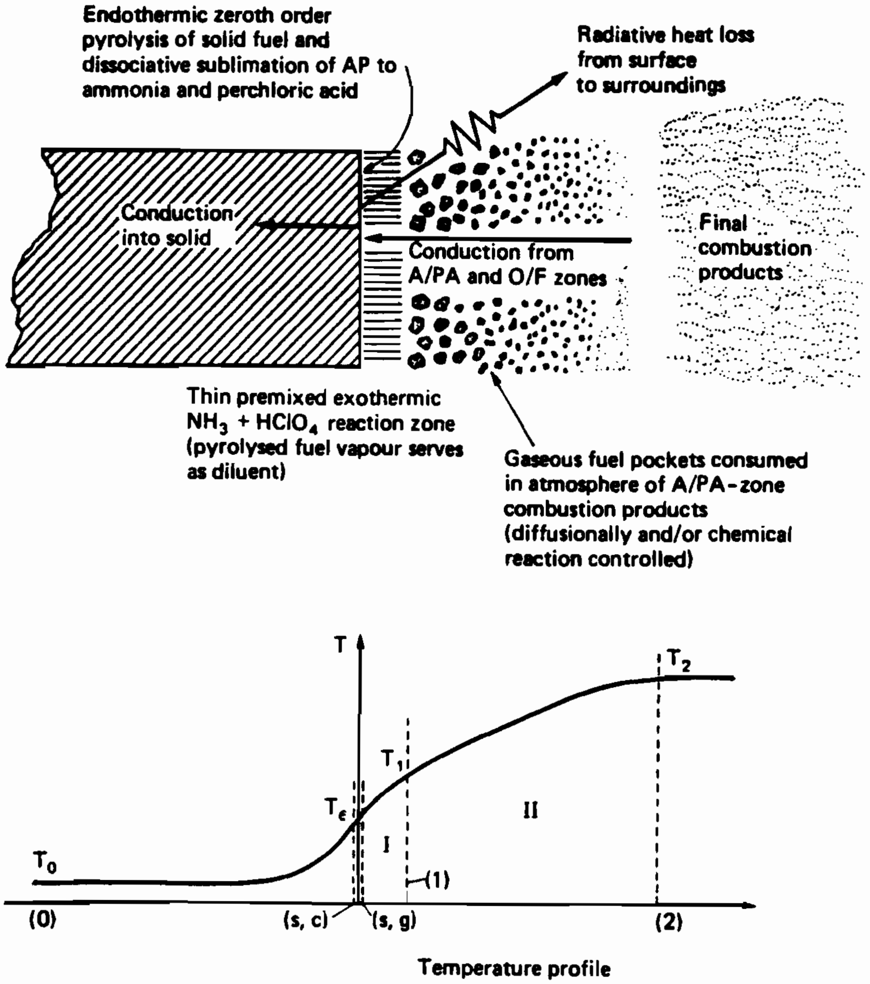


FIG. 129. Diffusion flame model for ammonium perchlorate composite propellants according to Steinz and Summerfield [23]. A/PA and O/F are ammonia perchloric acid and oxidant/fuel respectively.

$$(C_5H_5)_2Fe \longrightarrow Fe + 2\,C_5H_5.$$

Further discussion on burning composite propellants concerns the problems of inner ballistics and is therefore outside the scope of the present book.

MODIFICATIONS OF COMPOSITE PROPELLANTS

Modifications of composite propellants are mainly concerned with modification of the oxidizer. Ammonium nitrate (Vol. III, p. 383) is now less in use owing to such disadvantages as high hygroscopicity, relatively difficult ignitability and polymorphism at different temperatures combined with a change of density (see Chapter XVI).

Potassium perchlorate shows a high exponent $n = ca.\ 0.8$ in equation rate of burning/pressure. It also gives high temperature of burning which can readily produce corrosion of the nozzle.

The other perchlorates, such as hydrazinium, hydroxylaminium and nitronium perchlorates etc. are at present of theoretical interest only. Some of them (e.g. hydrazinium perchlorate) shows poor chemical stability and high sensitivity to mechanical shock.

Also hydrazinium nitrate does not seem to be a promising oxidizer.

MECHANICAL PROPERTIES

The mechanical properties of solid propellants are discussed by Kelly [25]. In the U.S.A. the methods are based on instructions worked out by a Joint—Army—Navy—Air Force (JANAF) Physical Properties Panel and include uniaxial and multiaxial measurements of mechanical strength.

They also include examination of the uniformity of the structure, detection of voids and cracks by X-ray examination.

The problems of testing mechanical properties are outside the chemical problems and are therefore not included in the present book.

MANUFACTURE OF COMPOSITE PROPELLANTS (Vol. III, p. 373)

The principles of the manufacture of composite propellants outlined in Vol. III are still valid. They are also described by Fluke [14] who gave a few schematic presentations for preparing the mixtures.

In principle they consist of:

(a) preparation of oxidizer (grinding, screening, mixing),
(b) binder and fuel preparation (polymerization),
(c) chamber insulation and lining,
(d) mixing of the propellant, casting into the chamber and lining,
(e) extraction of the grain from the chamber.

Mixing should be carried out in a kneading apparatus of the type shown in Figs 102 and 103. It should be done in a well defined sequence [16]. It is advisable to add ammonium perchlorate at the end after aluminium has been added. This is for safety reasons, as finely ground aluminium with ammonium perchlorate can form a dangerous dust when suspended in air.

Curing should not be carried out at a temperature above 80°C. After curing the extraction of the grains from the chamber can easily be done because of the shrinkage of the propellant mass.

Pneumatic mixing of ingredients developed by the Naval Propellant Plant was depicted in Vol. III, p. 390, Fig. 125.

As an illustration of mixing large charges, the following description can be given for preparing propellant for the shuttle's orbiter '*Columbia*'.

The formula is prepared in 7000 lb (*ca.* 3170 kg) batches at a remote complex in Utah operated by Thiokol Corp. The giant mixing bowl is of 2270 l. capacity. Mixing consists of the following steps: aluminium powder, PBAN (polybutadienacrylic acid–acrylonitrile) polymer and ferric oxide powder are mixed. Then the epoxy curing agent is added without mixing so as to delay the start of the curing reaction. The bowl containing this premix is transported by trailer to another building where ammonium perchlorate is added and blended by remote control for explosive properties of ammonium perchlorate and the operation should be considered as dangerous.

The mixing bowl is transferred to another site where the propellant is poured into casting segments. Each booster is built from four such segments assembled in a reusable steel casing. It takes 20 hours to fill one casting segment. The mixture is then cured at 57°C for four days and takes on the consistency of hard rubber.

SHAPES OF THE PROPELLANT GRAINS (Vol. III, p. 366)

A full description of possible shapes of grains and the pressure developed with time of burning has been given in a monograph [3] and is partly reproduced here – Fig. 130.

The most advantageous are shapes (2-cigarette burning), (3) and others (7–10) giving a constant or nearly constant pressure. Tube without inhibiting layers (4) and plain (1) are used when a high initial thrust is needed. Shape (5) and particularly (6) are much appreciated when a high thrust at the later stage of burning is required.

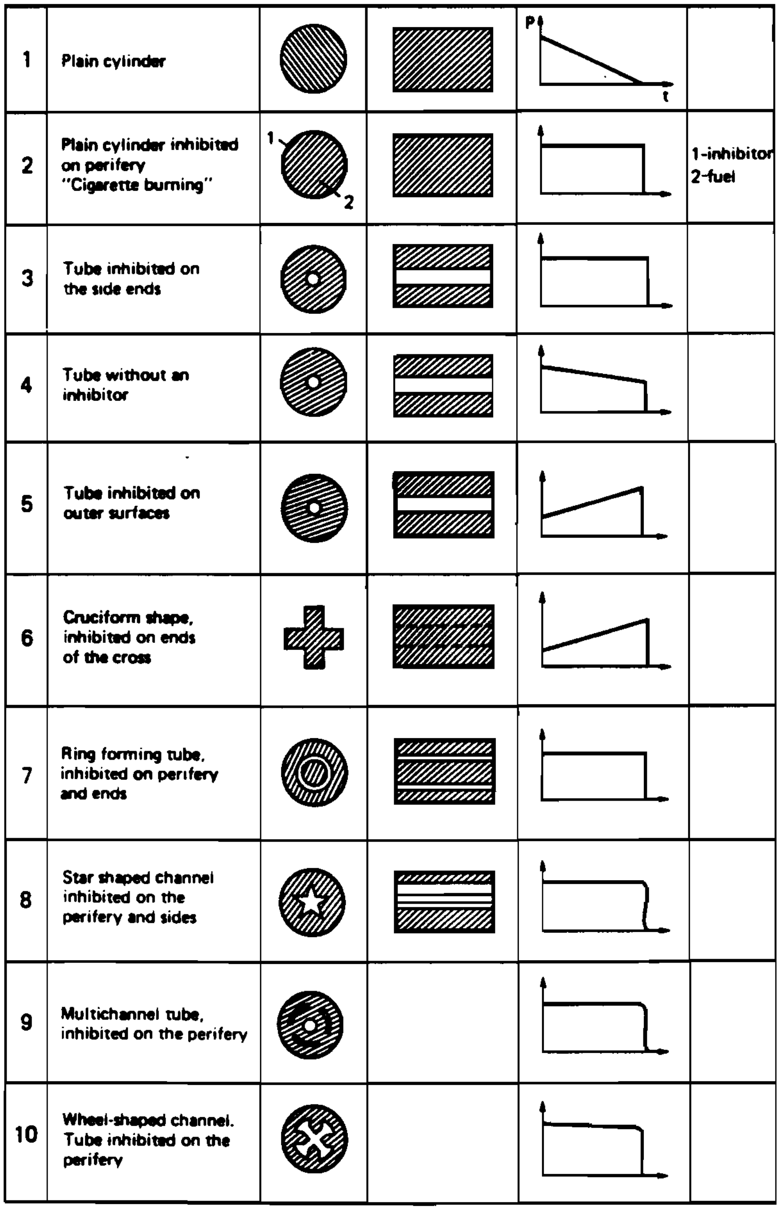
EXPLOSIVE PROPERTIES OF COMPOSITE PROPELLANTS (Vol. III, p. 393)

As mentioned in Vol. III, composite propellant detonate with difficulty because of their non-porous texture and very high density.

When in powdered form they behave as most explosives: sensitive to friction and impact and detonate readily when in low density.

According to information given in the Encyclopedia [1] the standard propellant made of ammonium perchlorate, PBAN and aluminium can detonate when RDX is added. Thus with 4.75, 7.1 and 9.2% the critical diameters were found to be: 28.2, 13.2 and 6.9 cm respectively. No rate of detonation was given.

Bernecker and Price [26] determined the rates of detonation of mixtures of ammonium perchlorate and wax (Table 126).



1	Plain cylinder	
2	Plain cylinder inhibited on perifery "Cigarette burning"	1-inhibitor 2-fuel
3	Tube inhibited on the side ends	
4	Tube without an inhibitor	
5	Tube inhibited on outer surfaces	
6	Cruciform shape, inhibited on ends of the cross	
7	Ring forming tube, inhibited on perifery and ends	
8	Star shaped channel inhibited on the perifery and sides	
9	Multichannel tube, inhibited on the perifery	
10	Wheel-shaped channel. Tube inhibited on the perifery	

FIG. 130. Shapes of grains and pressure against time of burning according to Krowicki and Syczewski [3].

TABLE 126. Rates of detonation of ammonium perchlorate–wax mixtures [26]

Composition NH_4ClO_4	Wax	Density	Diameter cm	Critical diameter cm	Rate of detonation m/sec
90	10	0.93	7.62	0.65–0.95	4070
		1.20	7.62	0.65–0.95	4540
		1.52	–	*ca.* 5	–
80	20	0.91	7.62	0.65–0.95	4480
		1.10	7.62	0.65–1.27	4790
		1.40		*ca.* 5	–

The above figures can give an approximate idea of the rates of detonation of ammonium perchlorate, PBAN and aluminium.

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CHAPTER 24

PROBLEMS OF SAFETY IN THE MANUFACTURE AND HANDLING OF EXPLOSIVES

The fact that explosive molecules are designed in such a way that they should burn, explode or detonate requires of course that their manufacture, handling and transportation should be carried out with special precautions.

Wide monographs recently appeared on problems of hazards and safety with explosives [14, 15].

MANUFACTURE

Precautions which are necessary in the processes of manufacturing explosives were described in the texts dedicated to their manufacture. However, there are a few principles common to all processes. These are:

Remote control of the functioning of production apparatus which should be provided with the elements connected to the remote control. The following are the most dangerous to manufacture:

(a) black powder,
(b) nitroglycerine and similar *O*-nitro compounds,
(c) initiating explosives and their mixtures.

Remote control ensures that not a single person is present in the proximity of the production apparatus.

There is however a danger when automation is not functioning correctly and has ceased to be reliable. This may lead to a disaster (e.g. an accident in Biazzi nitroglycerine plant in Bhandara, India in 1975) [1]. In this case automation became dangerous. There is always a need for human control in the functioning of automation.

The remote control of temperature is needed in the course of nitration as described in Chapters VI, VIII, XI, XII and in making initiating explosives and their mixing, mixing of commercial explosives (Chapter XX), making smokeless powder (Chapter XXII).

STATIC ELECTRICITY

A great danger exists wherever there is friction and this is through charging with static electricity which on discharging may produce ignition. There are dangerous parts of the manufacture of explosives from that point of view, such as mixing and kneading apparatus, rollers of double and treble-base powder, rotating drums (Vol. III, p. 625), in flowing flammable liquids through the pipes (Vol. III, p. 589) and air with flammable vapours (Vol. III, p. 607), compression of air containing flammable vapours in the course of extrusion of smokeless powder with a volatile solvent (Vol. III, p. 595), friction between the stream of air and the grains of propellants (Vol. III, p. 603), cutting, screening and blending of propellants.

A few monographs have appeared on static electricity and the danger connected with the discharge of it producing explosions of gas mixtures, inflammable dust or even inflammable liquids or solids. These are monographs by Freytag [2] and Haase [3]. Also a book by Gugan should be consulted [4].

The principal method of avoiding the danger of the discharge of the static electricity is to earth all parts of machinery which are subjected to friction.

A general method of avoiding an accumulation of static electricity incorporating substances conducting electricity into the explosive on condition that the manufacturing apparatus is earthed. Relatively high humidity of the atmosphere (wherever it is not harmful to the production [8], ionization of the atmosphere by irradiation with γ- or X-rays are other factors which help in avoiding the accumulation of static electricity [9].

The addition of conducting substances to explosives is a general method of preventing the charging of explosives with static electricity. The conducting substances comprise graphite (a particularly frequent component of smokeless powder Vol. III, p. 625), aluminium powder wherever it can be included in the composition of explosives without creating a new danger (it is known that the addition of aluminium to black powder gives dangerous compositions). Where neither of these substances can be included into the formulation of explosives, some organic conductors, usually CT-complexes (Charge–Transfer complexes) or ionic surface active agents can be added in a small proportion (below 0.5%). Addition of such surface active agents was recently recommended in a patent by Wielgus, Zdrojek and co-workers [10]. Surface active agents were earlier recommended [11] in the textile industry where the problem of static electricity is particularly important (through friction).

The recent facts on new conducting polymers [13] should be used to examine its action against the accumulation of static electricity, provided they are not harmful to the stability of the powder. Particularly interesting seem to be polyacetylene or poly-*p*-phenylene arsenic pentafluoride.

Conductive rubber (with graphite or Al dust) is highly recommended and often compulsory for the soles of workers' shoes, and conductive mats and carpets where certain explosives are handled.

The charging of smokeless powder was described in detail by Uetake and Sato [12]. See also Vol. III, pp. 542–543, 682, 684.

For one exceptional sensitivity of lead styphnate to static electricity and danger of discharge see Vol. III, pp. 217–218.

FOREIGN BODIES IN MIXING MACHINES

Foreign bodies present by accident or carelessness in mixing machines, such as kneaders have frequently been responsible for accidents. The otherwise safe kneaders of Drais, Biazzi, Werner and Pfleiderer can become a source of danger. A few accidents of this type have been described by Biasutti [1].

CONSTRUCTION OF EXPLOSIVE FACTORIES

There is currently a tendency to construct buildings for the manufacture and storage of explosives which could prevent the propagation of a shock wave and thus reduce the area of destruction. Such were heavy underground buildings for some time favoured in Germany (e.g. Vol. II, p. 122, Figs 62, 63).

According to Kaye [5] currently much in use are laced concrete walls (Fig. 131) forming a shock wave barrier, but more modern designs are those of 'suppressive structures'. They are made of new 'suppressive structures' of several layers of louvered and perforated plates of angle iron and 'z' bars. This allows controlled release of blast effects from a detonation within the structure. Subsequently a controlled release of blast effects occurs.

DETECTION OF HIDDEN EXPLOSIVES IN LUGGAGE

The increasing number of acts of terrorism particularly dangerous in airflights have made it necessary to find methods of detecting explosives hidden in luggage. Helf [6] gave a detailed description of the existing method, which consists in irradiating the luggage or suspect package with fast neutrones followed by the measurement of γ-irradiation from the activated explosive if present in the examined package. It is based on the assumption that most explosives contain nitrogen – usually greater than in items present in luggage.

Here is a description of the process as given by Helf: 'when an explosive is irradiated with fast neutrones a ^{14}N nucleus captures the incident fast neutron and ejects two slow neutrons. The resulting nucleus ^{13}N is radioactive and decays with a 10 min half-life to stable ^{13}C. In this last transition a positron β^+ is emitted. Because of its opposite charge, the β^+ is strongly attracted by the nearby electron; in the resulting collision, both the positron and electron are annihilated and in that process the masses of colliding particles are converted into two 0.511 MeV quanta of electromagnetic radiation.

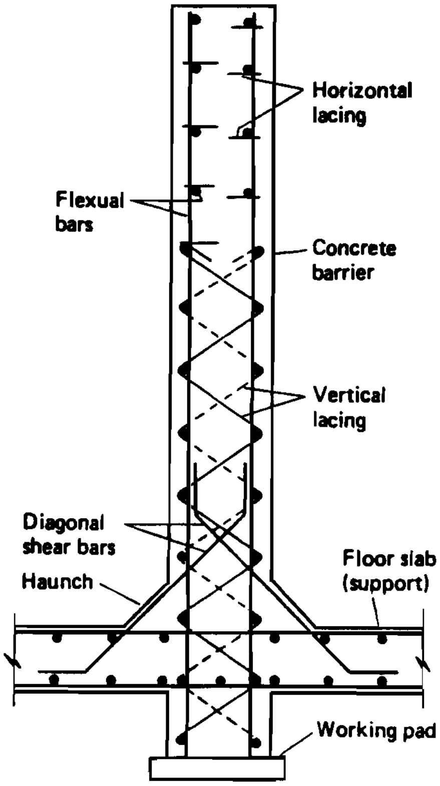

FIG. 131. Typical laced concrete wall according to Kaye [5].

These γ-rays are what are detected to indicate the possible presence of an explosive'.

Figure 132 gives a scheme of the functioning of the apparatus worked out by North American Rockwell Corp. (Los Angeles) 'A conveyer belt transports the luggage first past a neutron generator and then past a detector. The radiation detected is amplified, analysed and compared with a preset threshold. If the detected radiation surpasses the threshold, a visual alarm is activated'.

Both generator and detector should be heavily shielded by concrete and lead, to protect the environment from the harmful radiation.

The drawback of this system is in the fact that harmless substances containing nitrogen, such as wool and synthetic fibres can give a signal similar to that of explosives.

Picatinny Arsenal [6] developed a method of activating both nitrogen and oxygen considering that explosives contain a characteristic ratio N/O and thus lower the proportion of false alarms.

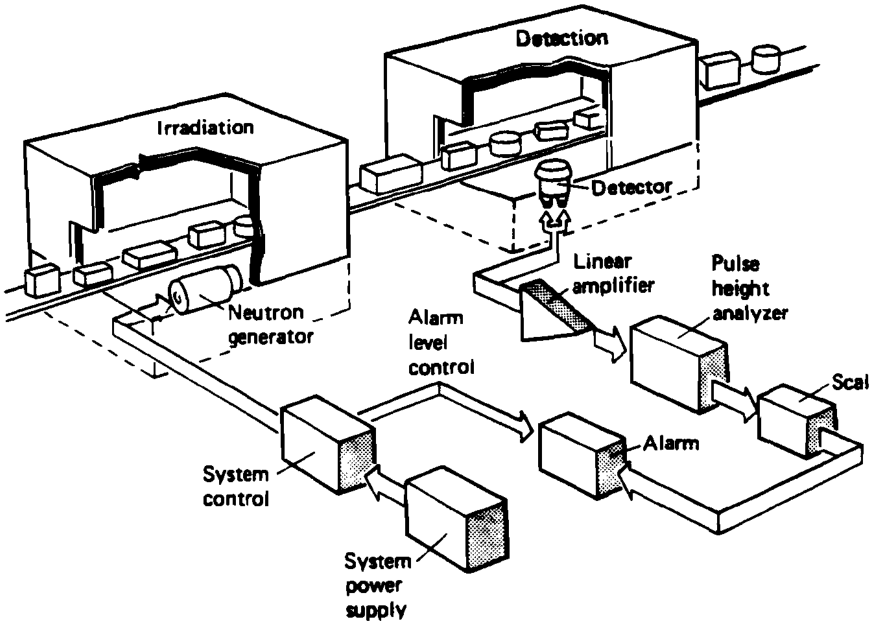

FIG. 132. Fast neutron activation system for the inspection of airline luggage for the presence of hidden explosives, according to Helf [6].

TAGGING OF COMMERCIAL EXPLOSIVES

It is now required in the United States that commercial explosives should be 'tagged' in such a way that the detection and post-detonation identification of explosives should be possible. Materials added to explosives for these purposes are called taggants.

The information on taggants was given by Boyars [7]. They are tiny coded particles added to explosives during their manufacture that 'can survive detonation in sufficient quantity to be recovered and decoded and, through distribution records, allow the explosives to be traced back to the last legal possessor. They are incorporated in quantities of 0.05% or less by the explosives manufacturers'.

They are made of a laminated melaminealkyd core encapsulated in polyethylene wax. The core is colour coded by the inclusion of pigments. One of the layers contains iron particles to make the taggant magnet-sensitive and one or both exterior layers contain fluorescent compounds which respond to ultraviolet radiation.

Obviously they should not increase the sensitivity to impact, friction and chemical (thermal) stability.

Two types of taggants are in use:

Type A (unencapsulated) and C (encapsulated).
Type B made of melamineacrylic resin is hard and has sensitized explosives, it seems not to be in use.

GENERAL DESCRIPTION OF SAFETY

A general description of safety in the manufacture, handling and storage of 'Reactive Chemicals' and mainly of explosives is described in a Japanese book [14]. It contains chapters on:

1. Fire and explosion hazards from reactive chemicals
2. Estimation of energy hazards
3. Computational prediction of explosion, deflagration and exothermic decomposition
4. Standard tests for reactive chemicals
5. Screening tests
6. Comprehensive evaluation
7. Activities of safety organization in various countries
8. Emergency response system for hazardous material
9. Earthquake countermeasures.

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CHAPTER 25

TOXICITY OF EXPLOSIVES

The toxicity of explosives was described in Vols I–III and more information has appeared recently as a result of the progress of toxicology and hygiene. Thus the former information needs some additions. An excellent review of the toxic properties of more important explosives was recently given by Rosenblatt [1]. Some information from this and other sources will be given below.

AROMATIC NITRO COMPOUNDS

m-Dinitrobenzene

The toxicity of this compound is of a great importance because of its intensity and also because of the importance of the substance as an intermediate in organic industry. The toxicity of *m*-DNB was described in Vol. I, pp. 240–242 and also in this volume: Chapter VI, refs [8, 82, 83]. Many fatal accidents have been attributed to poisoning by TNT were caused in fact by the impurities of TNT produced by the presence of small proportions of *m*-DNB. Rosenblatt [1] reported that 24,000 cases of poisoning with TNT were recorded during World War I and out of this 580 were fatal. During World War II the number of fatalities was only 22.

This should be attributed not only to better hygiene (as pointed out by Rosenblatt) but also to the higher purity of TNT, because of a higher purity of toluene used for the nitration.

As already pointed out (Vol. I, p. 240) dinitrobenzene affects haemoglobin and damages the liver.

2,4-Dinitrotoluene

This compound – an intermediate in the formation of TNT, can also be an impurity of TNT. The symptoms of poisoning are similar to poisoning with other nitro compounds the chief clinical findings are [1]: pallor, cyanosis and anaemia in which the blood cells are of normal size and contain normal amounts of haemoglobin. Patients recover from DNT poisoning after being treated in a DNT free atmosphere.

The lethal dose in rats (LD_{50}) was found to be 568–650 mg/kg. Dogs showed high sensitivity: doses 20–25 mg/kg/day were toxic in subchronic test which lasted 90 days, and in some cases were lethal. It was also found that 2,4-DNT is carcinogenic in mammalian animals.

2,4,6-Trinitrotoluene

TNT exposures can occur by inhalation of the dust, through ingestion and via skin absorption [1]. The action of TNT produces changes in blood: the red blood cells count and haemoglobin content decreases on longer exposure because the activity of the bone marrow is lowered. Another type of symptoms are due to atrophy of the liver. No carcinogenic effect has been recorded in men or animals.

The maximum permissible inhalation level in U.S.S.R. is 1.0 mg/m^3 and in the U.S.A. Army 0.5 mg/m^3.

The lethal dose by oral administration (LD_{50}) in rats is 820–1010 mg/kg.

Among metabolites in humans the following were identified: 4-amino- and 6-aminodinitrotoluene, tetranitroazoxytoluene, 2-hydroxylamino-4,6-dinitrotoluene, 2,4-diamino-6-nitro- and 2,6-diamino-4-nitrotoluene, 2,4,6-trinitrobenzoic acid. A former finding that TNT is toxic to fish has been confirmed.

'Red water' from the treatment of TNT with sodium sulphite is more toxic than TNT, this is mainly due to the presence of dinitrotoluene derivatives.

ALIPHATIC NITRO COMPOUNDS

2-Nitropropane

2-Nitropropane is being used extensively in the U.S.A. as a solvent. It was recently reported that prolonged exposure of rats to the action of 2-nitropropane can produce cancer [2].

Tetranitromethane

Experiments with animals show that inhalation of tetranitromethane can produce respiratory tract irritation and severe pneumonia but no methaemoglobinaemia [1].

NITRATE ESTERS

Methyl Nitrate [1]

The action is similar to nitroglycerine, but much weaker. Oral LD_{50} in rats was 344 mg/kg. Inhalation of 117 mg by humans induce headache.

Nitroglycerine [1]

It is known in medicine as a vasodilator and there is an extensive literature on its biochemical and clinical aspects. The most common dose is *ca.* 0.01 mg/kg. Chronic human exposure to NG produces a methemoglobinaemia and the development of tolerance to the drug. Withdrawal from frequent exposure to NG may cause severe headaches. The LD_{50} in rats is 822–884 mg/kg by oral administration. It is toxic to fish, e.g. LD_{50} 1.38 mg/l.

Nitrocellulose

Owing to the insolubility of nitrocellulose, no toxic effect has been found to experimental animals including fish.

NITRAMINES

Nitroguanidine

It is of very low toxicity. LD_{50} in rats was found to be 4640 mg/kg. [1].

Cyclonite (RDX, Hexogene)

More information has been collected on the toxicity of Cyclonite. Experiments with animals confirmed earlier findings on convulsions caused by Cyclonite. Important observations with humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident was recorded [3]. Rosenblatt [1] described acute intoxication of soldiers either chewing a plastic explosive C–4 containing 91% RDX or using it for cooking and inhaling the fumes. RDX intoxication involves gastrointestinal, central nervous system and renal effects. No liver involvement has been recorded and the cerebrospinal fluid was normal.

Acute toxicity in rats (LD_{50}) was determined: by oral administration 200 mg/kg and by intravenous and intraperitoneal administration: 18 mg/kg and 10 mg/kg respectively. Chronic toxicity by oral administration to rats gave variable results: in one series of experiments 10 mg/kg daily in rats for two years showed no toxic symptoms except a retarded weight in females. No carcinogenic effect was found.

In fish LD_{50} was found to be *ca.* 3.6 mg/l.

Octogene (HMX)

Very low solubility of HMX (as compared with RDX) makes experiments on toxicity of the compounds less conclusive than with RDX. So far it appears that HMX is less toxic than RDX [1].

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