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Thomas M. Klapötke

CHEMISTRY OF HIGH-ENERGY MATERIALS

2ND EDITION

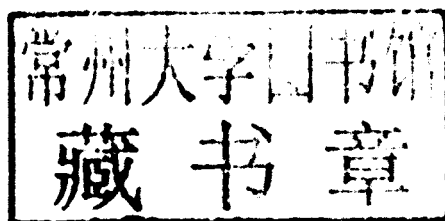


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This book contains 154 figures and 74 tables.

ISBN 978-3-11-027358-8
e-ISBN 978-3-11-027359-5

Library of Congress Cataloging-in-Publication Data

A CIP catalog record for this book has been applied for at the Library of Congress.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie;
detailed bibliographic data are available in the Internet at <http://dnb.dnb.de>.

© 2012 Walter de Gruyter GmbH & Co. KG, Berlin/Boston

Coverimage: Hemera/Thinkstock
Typesetting: Meta Systems GmbH, Wustermark
Printing and Binding: Hubert & Co., Göttingen
Printed in Germany
www.degruyter.com

Klapötke

Chemistry of High-Energy Materials
2nd Edition

“We will not waver; we will not tire; we will not falter;
and we will not fail. Peace and freedom will prevail.”

*G. W. Bush,
Presidential Address to the Nation,
October 7th 2001*

Preface to this 2nd English edition

Everything said in the preface to the first German and first English editions still holds and essentially does not need any addition or correction. In this revised second edition in English we have up-dated the manuscript and added some recent aspects of energetic materials:

- (i) We have tried to correct some mistakes which can not be avoided in a first edition and also updated the references where appropriate.
- (ii) The chapters on Ionic Liquids, Primary Explosives, NIR formulations, Smoke Compositions and High-Nitrogen Compounds were updated.
- (iii) Two new short chapters on Co-Crystallization (9.5) and Future Energetic Materials (9.6) have been added.

In addition to the people thanked in the German and first English edition, the author would like to thank Dr. Jesse Sabatini and Dr. Karl Oyler (ARDEC, Picatinny Arsenal, NJ) for many inspired discussions concerning pyrotechnics.

Munich, May 2012

Thomas M. Klapötke

Preface to the first English edition

Everything said in the preface to the first German edition remains valid and essentially does not need any addition or correction. There are several reasons for translating this book into English:

- The corresponding lecture series at LMU is now given in English in the post-graduate M.Sc. classes, to account for the growing number of foreign students and also to familiarize German students with the English technical terms.
- To make the book available to a larger readership world-wide.
- To provide a basis for the author's lecture series at the University of Maryland, College Park.

We have tried to correct some omissions and errors which can not be avoided in a first edition and have also updated the references where appropriate. In addition, five new chapters on Combustion (Ch. 1.4), NIR formulations (Ch. 2.5.5), the Gurney Model (Ch. 7.3), dinitroguanidine chemistry (Ch. 9.4) and nanothermites (Ch. 13.3) have been included in the English edition. The chapter on calculated combustion parameters (Ch. 4.2.3) has been extended.

In addition to the people thanked in the German edition, the author would like to thank Dr. Ernst-Christian Koch (NATO, MSIAC, Brussels) for pointing out various mistakes and inconsistencies in the first German edition. For inspired discussions concerning the Gurney model special thanks goes to Joe Backofen (BRIGS Co., Oak Hill). Dr. Anthony Bellamy, Dr. Michael Cartwright (Cranfield University), Neha Mehta, Dr. Reddy Damavarapu and Gary Chen (ARDEC) and Dr. Jörg Stierstorfer (LMU) are thanked for ongoing discussions concerning secondary and primary explosives.

The author also thanks Mr. Davin Piercey, B.Sc. for corrections and for writing the new chapter on nanothermites, Dr. Christiane Rotter for her help preparing the English figures and Dr. Xaver Steemann for his help with the chapter on detonation theory and the new combustion chapter. The author thanks the staff of de Gruyter for the good collaboration preparing the final manuscript.

Munich, January 2011

Thomas M. Klapötke

Preface to the first German edition

This book is based on a lecture course which has been given by the author for more than 10 years at the Ludwig-Maximilian University Munich (LMU) in the post-graduate Master lecture series, to introduce the reader to the chemistry of highly energetic materials. This book also reflects the research interests of the author. It was decided to entitle the book “Chemistry of High-Energy Materials” and not simply “Chemistry of Explosives” because we also wanted to include pyrotechnics, propellant charges and rocket propellants into the discussion. On purpose we do not give a comprehensive historical overview and we also refrained from extensive mathematical deductions. Instead we want to focus on the basics of chemical explosives and we want to provide an overview of recent developments in the research of energetic materials.

This book is concerned with both the civil applications of high-energy materials (e.g. propellants for carrier or satellite launch rockets and satellite propulsion systems) as well as the many military aspects. In the latter area there have been many challenges for energetic materials scientists in recent days some of which are listed below:

- In contrast to classical targets, in the on-going global war on terror (GWT), new targets such as tunnels, caves and remote desert or mountain areas have become important.
- The efficient and immediate response to time critical targets (targets that move) has become increasingly important for an effective defense strategy.
- Particularly important is the increased precision (“we want to hit and not to miss the target”, Adam Cumming, DSTL, Sevenoaks, U.K.), in order to avoid collateral damage as much as possible. In this context, an effective coupling with the target is essential. This is particularly important since some evil regimes often purposely co-localize military targets with civilian centers (e.g. military bases near hospitals or settlements).
- The interest in insensitive munitions (IM) is still one of the biggest and most important challenges in the research of new highly energetic materials.
- The large area of increasing the survivability (for example by introducing smokeless propellants and propellant charges, reduced signatures of rocket motors and last but not least, by increasing the energy density) is another vast area of huge challenge for modern synthetic chemistry.
- Last but not least, ecological aspects have become more and more important. For example, on-going research is trying to find suitable lead-free primary explosives in order to replace lead azide and lead styphnate in primary composi-

tions. Moreover, RDX shows significant eco- and human-toxicity and research is underway to find suitable alternatives for this widely used high explosive. Finally, in the area of rocket propulsion and pyrotechnical compositions, replacements for toxic ammonium perchlorate (replaces iodide in the thyroid gland) which is currently used as an oxidizer are urgently needed. Despite all this, the performance and sensitivity of a high-energy material are almost always the key-factors that determine the application of such materials – and exactly this makes research in this area a great challenge for synthetically oriented chemists.

The most important aspect of this book and the corresponding lecture series at LMU Munich, is to prevent and stop the already on-going loss of experience, knowledge and know-how in the area of the synthesis and safe handling of highly energetic compounds. There is an on-going demand in society for safe and reliable propellants, propellant charges, pyrotechnics and explosives in both the military and civilian sector. And there is no one better suited to provide this expertise than well trained and educated preparative chemists.

Last but not least, the author wants to thank those who have helped to make this book project a success. For many inspired discussions and suggestions the authors want to thank the following colleagues and friends: Dr. Betsy M. Rice, Dr. Brad Forch and Dr. Ed Byrd (US Army Research Laboratory, Aberdeen, MD), Prof. Dr. Manfred Held (EADS, TDW, Schrobenhausen), Dr. Ernst-Christian Koch (NATO MSIAC, Brussels), Dr. Miloslav Krupka (OZM, Czech Republic), Dr. Muhamed Sucasca (Brodarski Institute, Zagreb, Croatia), Prof. Dr. Konstantin Karaghiosoff (LMU Munich), Prof. Dr. Jürgen Evers (LMU Munich), as well as many of the past and present co-workers of the authors research group in Munich without their help this project could not have been completed.

The author is also indebted to and thanks Dipl.-Chem. Norbert Mayr (LMU Munich) for his support with many hard- and soft-ware problems, Ms. Carmen Nowak and Ms. Irene S. Scheckenbach (LMU Munich) for generating many figures and for reading a difficult manuscript. The author particularly wants to thank Dr. Stephanie Dawson (de Gruyter) for the excellent and efficient collaboration.

Munich, July 2009

Thomas M. Klapötke

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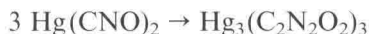
1 Introduction

1.1 Historical Overview

In this chapter we do not want to be exhaustive in scope, but rather to focus on some of the most important milestones in the chemistry of explosives (Tab. 1.1). The development of energetic materials began with the accidental discovery of **blackpowder** in China (~ 220 BC). In Europe this important discovery remained dormant until the 13th and 14th centuries, when the English monk Roger Bacon (1249) and the German monk Berthold Schwarz (1320) started to research the properties of blackpowder. At the end of the 13th century, blackpowder was finally introduced into the military world. However, it was not until 1425 that Corning greatly improved the production methods and blackpowder (or gunpowder) was then introduced as a propellant charge for smaller and later also for large calibre guns.

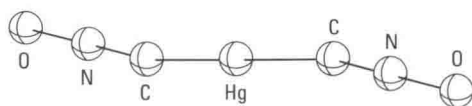
The next milestone was the first small-scale synthesis of **nitroglycerine (NG)** by the Italian chemist Ascanio Sobrero (1846). Later, in 1863 Imanuel Nobel and his son Alfred commercialized NG production in a small factory near Stockholm (Tab. 1.1). NG is produced by running highly concentrated, almost anhydrous, and nearly chemically pure glycerine into a highly concentrated mixture of nitric and sulfuric acids ($\text{HNO}_3/\text{H}_2\text{SO}_4$), while cooling and stirring the mixture efficiently. At the end of the reaction, the nitroglycerine and acid mixture is transferred into a separator, where the NG is separated by gravity. Afterwards, washing processes using water and alkaline soda solution remove any residual acid.

Initially NG was very difficult to handle because of its high impact sensitivity and unreliable initiation by blackpowder. Among many other accidents, one explosion in 1864 destroyed the Nobel factory completely, killing Alfred's brother Emil. In the same year, Alfred Nobel invented the metal blasting cap detonator, and replaced blackpowder with **mercury fulminate (MF)**, $\text{Hg}(\text{CNO})_2$. Although the Swedish-German Scientist Johann Kunkel von Löwenstern had described $\text{Hg}(\text{CNO})_2$ as far back as in the 17th century, it did not have any practical application prior to Alfred Nobel's blasting caps. It is interesting to mention that it was not until the year 2007 that the molecular structure of $\text{Hg}(\text{CNO})_2$ was elucidated by the LMU research team (Fig. 1.1) [1, 2]. Literature also reports the thermal transformation of MF, which, according to the below equation, forms a new mercury containing explosive product which is reported to be stable up to 120 °C.



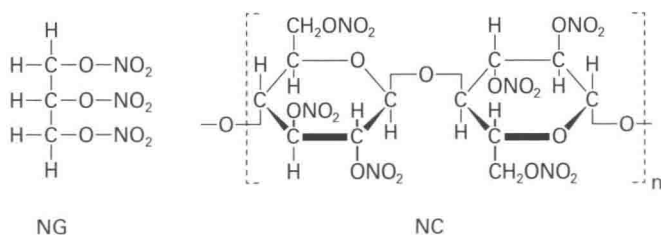
Tab. 1.1 Historical overview of some important secondary explosives.

substance	acronym	development	application	density/g cm ⁻³	explosive power ^a
blackpowder	BP	1250–1320	1425–1900	ca. 1.0	
nitroglycerine	NG	1863	in propellant charges	1.60	170
dynamite	Dy	1867	civil/commercial only	varies	varies
picric acid	PA	1885–1888	WW I	1.77	100
nitroguanidine	NQ	1877	most in TLPs	1.71	99
trinitrotoluene	TNT	1880	WW I	1.64	116
nitropenta	PETN	1894	WW II	1.77	167
hexogen	RDX	1920–1940	WW II	1.81	169
octogen	HMX	1943	WW II	1.91	169
				(β polymorph)	
hexanitrostilbene	HNS	1913	1966	1.74	
triaminotrinitrobenzene	TATB	1888	1978	1.93	
HNIW	CL-20	1987	under evaluation	2.1	
				(ϵ polymorph)	

^a rel. to PA**Fig. 1.1** Molecular structure of mercury fulminate, $\text{Hg}(\text{CNO})_2$.

After another devastating explosion in 1866 which completely destroyed the NG factory, Alfred Nobel focused on the safe handling of NG explosives. In order to reduce the sensitivity, Nobel mixed NG (75%) with an absorbent clay called “Kieselguhr” (25%). This mixture called “Guhr Dynamite” was patented in 1867. Despite the great success of dynamite in the civil sector, this formulation has never found significant application or use in the military sector.

One of the great advantages of NG (Fig. 1.2) in comparison to blackpowder (75% KNO_3 , 10% S_8 , 15% charcoal) is that it contains both the fuel and oxidizer

**Fig. 1.2** Molecular structures of nitroglycerine (NG) and nitrocellulose (NC).

in the same molecule which guarantees optimal contact between both components, whereas in blackpowder, the oxidizer (KNO_3) and the fuel (S_8 , charcoal) have to be physically mixed.

At the same time as NG was being researched and formulated several other research groups (Schönbein, Basel and Böttger, Frankfurt-am-Main) worked on the nitration of cellulose to produce **nitrocellulose (NC)**. In 1875 Alfred Nobel discovered that when NC is formulated with NG, they form a gel. This gel was further refined to produce blasting gelatine, gelatine dynamite and later in 1888 ballistite (49% NC, 49% NG, 2% benzene and camphor), which was the first smokeless powder. (Cordite which was developed in 1889 in Britain, had a very similar composition.) In 1867 it was proven that mixtures of NG or dynamite and ammonium nitrate (AN) showed enhanced performance. Such mixtures were used in the civil sector. In 1950 manufacturers started to develop explosives which were waterproof and solely contained the less hazardous AN. The most prominent formulation was ANFO (Ammonium Nitrate Fuel Oil) which found extensive use in commercial areas (mining, quarries etc.). Since the 1970s aluminium and monomethylamine were added to such formulations to produce gelled explosives which could detonate more easily. More recent developments include production of emulsion explosives which contain suspended droplets of a solution of AN in oil. Such emulsions are water proof, yet readily detonate because the AN and oil are in direct contact. Generally, emulsion explosives are safer than dynamite and are simple and cheap to produce.

Picric acid (PA) was first reported in 1742 by Glauber, however it was not used as an explosive until the late 19th century (1885–1888), when it replaced blackpowder in nearly all military operations world-wide (Fig. 1.3). PA is prepared best by dissolving phenol in sulfuric acid and the subsequent nitration of the resulting of phenol-2,4-disulfonic acid with nitric acid. The direct nitration of phenol with nitric acid is not possible because the oxidizing HNO_3 decomposes the phenol molecule. Since the sulfonation is reversible, the $-\text{SO}_3\text{H}$ groups can then be replaced with $-\text{NO}_2$ groups by refluxing the disulfonic acid in concentrated nitric acid. In this step the third nitro group is introduced as well. Although pure PA can be handled safely, a disadvantage of PA is its tendency to form impact sensitive metal salts (picrates, primary explosives) when in direct contact with shell walls. PA was used as a grenade and as mine filling.

Tetryl was developed at the end of the 19th century (Fig. 1.3) and represents the first explosive of the nitroamino (short: nitramino) type. Tetryl is best obtained by dissolving monomethylaniline in sulfuric acid and then pouring the solution into nitric acid, while cooling the process.

The above mentioned disadvantages of PA are overcome by the introduction of **trinitrotoluene (TNT)**. Pure 2,4,6-TNT was first prepared by Hepp (Fig. 1.3) and its structure was determined by Claus and Becker in 1883. In the early 20th century TNT almost completely replaced PA and became the standard explosive during WW I. TNT is produced by the nitration of toluene with mixed nitric and sulfuric acid. For military purposes TNT must be free of any isomer other than the 2,4,6-

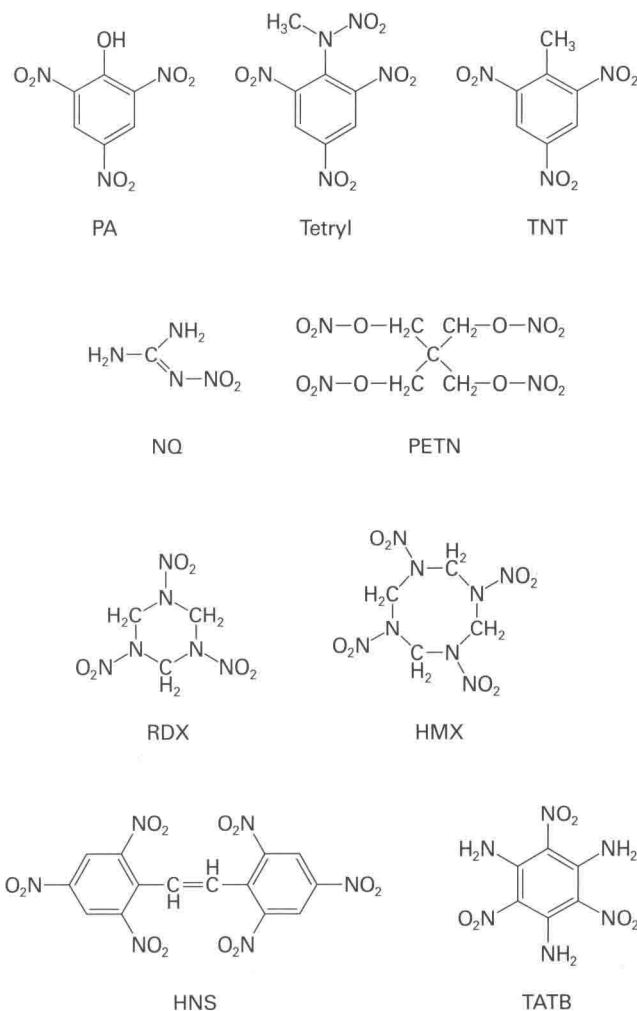
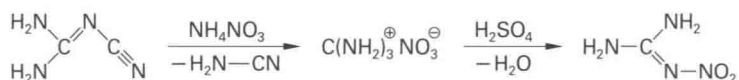


Fig. 1.3 Molecular structures of picric acid (PA), tetryl, trinitrotoluene (TNT), Nitroguanidine (NQ), pentaerythritol tetranitrate (PETN), hexogen (RDX), octogen (HMX), hexanitrostilbene (HNS) and triaminotrinitrobenzene (TATB).

isomer. This is achieved by recrystallization from organic solvents or from 62% nitric acid. TNT is still one of the most important explosives for blasting charges today. Charges are produced through casting and pressing. However, cast charges of TNT often show sensitivity issues and do not comply with the modern insensitive munition requirements (IM). For this reason alternatives to TNT have been suggested. One of these replacements for TNT is NTO (filler) combined with 2,4-dinitroanisole (DNAN, binder).

Nitroguanidine (NQ) was first prepared by Jousselin in 1887 (Fig. 1.3). However, during WW I and WW II it only found limited use, for example in formulations

with AN in grenades for mortars. In more recent days NQ has been used as a component in triple-base propellants together with NC and NG. One advantage of the triple-base propellants is that unlike double-base propellants the muzzle flash is reduced. The introduction of about 50% of NQ to a propellant composition also results in a reduction of the combustion temperature and consequently reduced erosion and increased lifetime of the gun. NQ can be prepared from dicyandiamide and ammonium nitrate via guanidinium nitrate which is dehydrated with sulfuric acid under the formation of NQ:



The most widely used explosives in WW II other than TNT were hexogen (RDX) and pentaerythritol tetranitrate (nitropenta, PETN) (Fig. 1.3). Since PETN is more sensitive and chemically less stable than RDX, RDX was (and is) the most commonly used high explosive. PETN is a powerful high explosive and has a great shattering effect (brisance). It is used in grenades, blasting caps, detonation cords and boosters. PETN is not used in its pure form because it is too sensitive. A formulation of 50% TNT and 50% PETN is known as “pentolite”. In combination with plasticized nitrocellulose PETN is used to form polymer bonded explosives (PBX). The military application of PETN has largely been replaced by RDX. PETN is prepared by introducing pentaerythritol into concentrated nitric acid while cooling and stirring the mixture efficiently. The then formed bulk of PETN crystallizes out of the acid solution. The solution is then diluted to about 70% HNO_3 in order to precipitate the remaining product. The washed crude product is purified by recrystallization from acetone.

Hexogen (RDX) was first prepared in 1899 by Henning for medicinal use. (N.B. NG and PETN are also used in medicine to treat angina pectoris. The principal action of these nitrate esters is vasodilation (i.e. widening of the blood vessels). This effect arises because in the body the nitrate esters are converted to nitric oxide (NO) by mitochondrial aldehyde dehydrogenase, and nitric oxide is a natural vasodilator.) In 1920 Herz prepared RDX for the first time by the direct nitration of hexamethylene tetramine. Shortly afterwards Hale (Picatinny Arsenal, NJ) developed a process that formed RDX in 68% yield. The two processes most widely used in WW II were

1. the Bachmann process (KA process) in which hexamethylene tetramine dinitrate reacts with AN and a small amount of nitric acid in an acetic anhydride medium to form RDX (type B RDX). The yields are high, however, 8–12% of HMX form as a side product.
2. the Brockman process (type A RDX) essentially produces pure RDX.

After WW II **octogen (HMX)** started to become available. Until today, most high explosive compositions for military use are based on TNT, RDX and HMX (Tab. 1.2).