

Methods for obtaining octogen (HMX)

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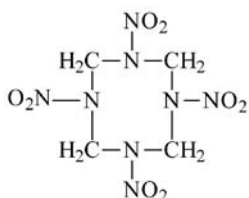
Introduction

Octogen - cyclotetramethylene-tetranitramine (HMX), is a powerful high brisant explosive manufactured in Poland having a high detonation velocity and featuring high thermal stability. Thanks to its high performance characteristics this explosive is widely used both in military and civil applications. Poland is one of the few countries where octogen is produced on an industrial scale. The production is carried out according to the original method developed by the Institute of Industrial Organic Chemistry in Warsaw. The institute carries out further research focused on synthesising the compound.

Octogen characteristic

Chemical name: 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine

Structural formula:



Summary formula: $C_4H_8N_8O_8$

Octogen (HMX) is a crystalline white-coloured solid. It occurs in four polymorphic crystal forms: alpha, beta, gamma, and delta, having different physical properties. The only one used in industrial applications is the beta form of octogen, stable at room temperature. For the first time, octogen was identified as a contaminant of hexogen. It was in the 1960s that more attention was paid to octogen after detecting better results for armour piercing with high-explosive anti-tank warheads (HEAT) shells filled with octogen as compared with hexogen (RDX). The use of octogen in explosive mixtures improves the detonation velocity, brisance and thermal stability. The calculated heat of explosion is 5679 J/g. The detonation velocity for octogen at a density of 1.84 g/cm³ is 9124 m/sec. The explosive's work capacity (strength) measured in the Trauzl lead block test amounted to 145% of trinitrotoluene (TNT) value. Octogen shows strong thermal resistance, as its melting point ranges from 278.5°C to 280°C.

Methods for obtaining octogen (HMX)

Octogen (HMX) is obtained mainly in the nitration of hexamethylenetetramine. Both octogen and hexogen are produced from the same raw materials, while the difference in explosive effect depends on the proportion, sequence of feeding and the temperature conditions of synthesis. The nitration of hexamethylenetetramine under severe conditions leads to forming mainly a six-segment cyclic polynitrosamine – hexogen (RDX). Under milder conditions an eight-segment polynitrosamine compound is obtained – octogen. The temperature and environmental conditions of synthesis in most cases lead to production of octogen in its polymorphic alpha form, which in industrial processes requires conversion from the alpha to beta form.

The intermediate product of the hexamethylenetetramine nitration aimed at obtaining octogen is DPT (dinitro pentamethylene tetramine)

There are a few alternatives of the octogen synthesis:

- Direct, single-stage synthesis from hexamethylenetetramine
- Two-stage octogen synthesis from hexamethylenetetramine with the formation of an intermediate product (DPT)
- Two-stage octogen synthesis from hexamethylenetetramine without the formation of an intermediate product (DPT).

There are also methods using other initial substances than hexamethylenetetramine to obtain octogen and DPT, though they are of no practical importance.

Most known methods for obtaining octogen require the presence of acetic acid and acetic anhydride.

Below we present two different methods for producing octogen developed by the Institute of Industrial Organic Chemistry in Warsaw.

The two-stage synthesis of octogen from hexamethylenetetramine with the liberation of an intermediate product (DPT) without the presence of acetic acid and its anhydride

The method for obtaining octogen consists in two-stage synthesis with the liberation of an intermediate product - DPT.

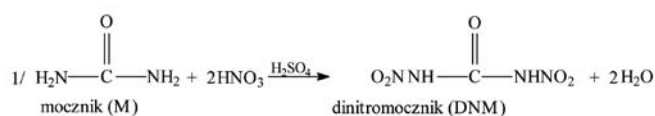
The first stage consists in obtaining DPT as a result of the following reactions:

- the nitration of urea
- the reaction of dinitrourea (DNU) with hexamethylenetetramine (HMTA)
- the cyclisation of linear nitrosamines with ammonia to form DPT

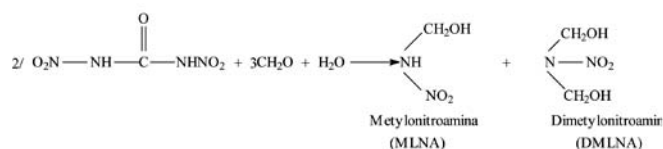
The second stage consists in obtaining HMX as a result of the following reactions:

- the nitrolysis of DPT
- the so-called oxidising crystallisation.

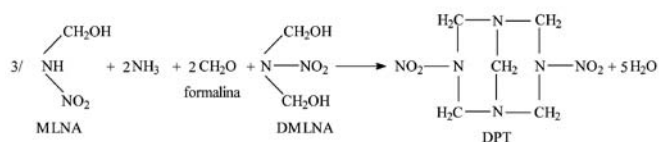
The main reaction taking place during the nitration of urea is the following:



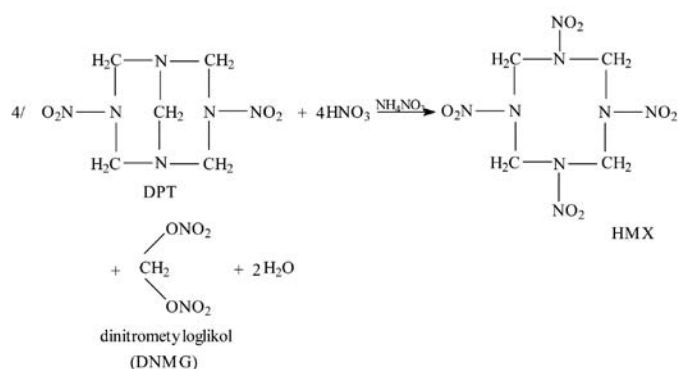
In the next stage dinitrourea (DNU) reacts with hexamethylenetetramine (HMTA), to be precise, with formaldehyde formed from hexamethylenetetramine (HMTA):



The cyclisation of linear nitrosamines runs in the following reaction:



The main reaction running during the nitrolysis of DPT looks as follows:



In addition to reactions leading to octogen formation there are a lot of side reactions leading to the formation of small amounts of hexogen, a number of linear nitrosamine and gaseous products (including CO_2 and N_2O).

During the stage of oxidising crystallisation the linear products decompose with the liberation of gaseous products – nitric oxides and carbon dioxide.

Stage 1 – the synthesis of DPT begins with the nitration of urea by using a nitrating mixture consisting of nitric acid and oleum (fuming sulphuric acid). The nitration of urea is carried out by proportioning urea to the nitrating mixture while stirring and cooling intensely the reacting material. Once the proportioning is completed, the reacting material is stirred to complete the process of nitration. Then, the nitrated material is proportioned to the already prepared water solution of hexamethylenetetramine (HMTA) while stirring intensely throughout the process. Once the operation is completed, the material is cooled down; then, the proportioning of 25 % aqueous ammonia solution begins and continues until the preset pH is reached. Finally, the DPT suspension formed is filtered. After completing filtration, the DPT is rinsed with water and dried.

Stage 2 of the production process consists in obtaining octogen by the nitrolysis of DPT.

The reaction is carried out by proportioning (adding) DPT to the nitrating mixture, constituting the solution of ammonium nitrate in concentrated nitric acid. The nitration is carried out at low temperature by intensely stirring and cooling the material. Then, the so-called oxidising crystallisation is carried out to precipitate the product and decompose by-products, by diluting nitrated material with water at elevated temperature. Water is added to keep the concentration of waste acids within the range of 50–55 %. This reaction consists in introducing water and reacting material into a reactor at the same time stirring it intensely, keeping the temperature required and cooling or heating the reacting material as necessary. The products of decomposition, i.e. the dark brown mixture of nitric oxides, are extracted and absorbed in water to obtain dilute nitric acid. Once the dilution process is completed, the suspension of octogen in acid is cooled down and delivered to a filter. The filtered, sour octogen is rinsed with water and dried.

The first stage is carried out periodically, while the second one is a continuous process.

With this method one obtains the final product having the main ingredient content of (the stable beta polymorphic form) more than 98 %, at a percentage yield of approximately 40 % (per hexamethylenetetramine (HMTA) volume).

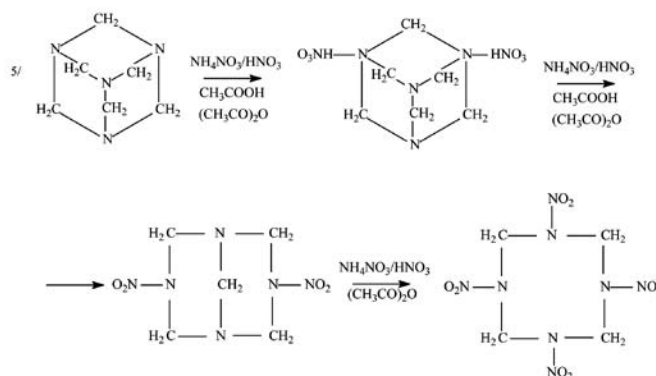
Zakłady Chemiczne “Nitro-Chem” SA (“Nitro-Chem” SA Chemical Plant) in Bydgoszcz has built a testing production process installation for manufacturing octogen with this method. After verifying the method under industrial conditions, the plant started the production of this explosive.

The two-stage synthesis of octogen from hexamethylenetetramine without the liberation of an intermediate product (DPT) with the presence of acetic acid and its anhydride

In this method octogen is obtained by a two-stage nitrolysis of hexamethylenetetramine (HMTA) in acetic acid, using the solution of ammonium nitrate in nitric acid, in the presence of acetic anhydride and trioxane (a trimer of formaldehyde).

The process is carried out continuously without the separation of an intermediate product - DPT.

The reaction of product formation looks as follows:



In addition to the main reaction leading to octogen formation there are a number of side reactions including the formation of hexogen and linear nitrosamines.

The process is carried out in equipment that consists of many reactors arranged in a cascade system. The first reactor is fed with:

- the solution of hexamethylenetetramine (HMTA) with troxane added, in acetic acid
- the solution of ammonium nitrate in nitric acid
- acetic anhydride.

In this apparatus an intermediate product is obtained – DPT. The reacting material is delivered into another unit where the reaction continues at high temperature (heating the material). Then, the material is directed to another unit where the following ingredients are proportioned (added):

- the solution of ammonium nitrate in nitric acid
- acetic anhydride.

The reaction of forming HMX in the nitrolysis of DPT occurs in this reactor. From there the material is fed to another apparatus where it is subject to heating. After leaving this reactor the post-reaction suspension goes to another unit where it is cooled down to approximately 20C and then the precipitate of raw HMX is filtered.

The raw product, subject to the nitrolysis according to this method, precipitates in its non-stable polymorphic alpha form. As a result of the synthesis, carried out under the conditions described above, we obtain a product that after stabilisation contains more than 98 % of pure octogen at a percentage yield of approx. 70 % per hexamethylenetetramine (HMTA) volume.

This method was used to perform some successfully completed industrial scale tests, i.e. the product obtained met the requirements assumed.

However, the method produces extremely large amounts of (approx. 18.8 kg per 1 kg of raw octogen) waste acetic acid at a concentration of approx. 50%. It was predicted that it would be subject to denitration and concentration and then it would be delivered back to the process. After completing offer-based installation tests concerning the installation for concentrating acetic acid, the concept was aborted and the research work on this octogen production method ended.

Summary

The process of obtaining octogen is complex as it forms a lot of different products from the same raw materials, which seems especially disadvantageous when the process is carried out on an industrial scale. Therefore, it is worth emphasizing that this was in Poland where the original method of octogen production had been developed and implemented.

Zygmunt MATYS - Eng., graduated from the Faculty of Chemistry of the Warsaw University of Technology. He is the author of 17 papers and 6 patents. He has taken part in a number of conferences and symposia both in Poland and abroad. He has been working at the Institute of Industrial Organic Chemistry for many years, dealing mainly with the synthesis and production process of explosives.

Dorota POWAŁA - Ph.D., (Eng), graduated from the Faculty of Chemistry of the Warsaw University of Technology (2001). She defended her doctoral dissertation at the Central Mining Institute (2010). Currently she works at the Institute of Industrial Organic Chemistry at the Department of High Explosives. Her research interests include explosive production process and testing. She is the co-author of 41 publications, 19 papers and posters presented at conferences held in Poland and abroad.

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Andrzej MARANDA – Professor (Ph.D., Eng), graduated from the Faculty of Chemistry at the Warsaw University of Technology (1971). Nowadays, he is working at the Military University of Technology and the Institute of Industrial Organic Chemistry. Research interests: chemistry, technology and application of explosives, environmental protection. He is an author and a co-author of five monographs, 20 patents, more than 500 articles, papers and posters presented at national and international conferences

Closing Ceremony of the Year of Maria Skłodowska-Curie

Three Nobel laureates in chemistry, representatives of Polish and French presidents, members of the Polish and French Academy of Sciences and Maria Skłodowska-Curie's grandson attended the closing ceremony the year of the Polish scientist.

Prof. Yonath added that she was particularly moved, when the Polish Ambassador to Israel organized a banquet on the occasion of Polish Independence Day on 144 birthday anniversary of Maria Skłodowska-Curie. During the ceremony, the Nobel Prize winner received Maria Skłodowska-Curie Medal, awarded by the Polish Chemical Society. The prof. Tseh Lee Yuan of Taiwan, who received Nobel Prize in 1986 for his contribution to the study the dynamics of elementary chemical processes, said that although his ancestors did not come from Poland, he always feels at home here, and that also for him Maria Skłodowska Curie was an inspiration in education and research. 1987 Nobel Prize winner Prof. Jean-Marie Lehn, considered one of the fathers of supramolecular chemistry, talked about esteem Skłodowska-Curie had among French scientists, particularly chemists. Skłodowska-Curie's granddaughter, Professor of nuclear physics Helene Langevin-Joliot, reminded that for many women her grandmother was primarily one of the first feminists, who in the scientific world dominated by men, made fundamental discoveries and received the highest honours. Prof. Langevin-Joliot received the Medal of the Polish Radiation Research Society. The ceremony was also attended by the grandson of Maria Skłodowska-Curie and Pierre Curie, biologist Prof. Pierre Joliot and his wife, the President of the Polish Academy of Sciences, Prof. Michał Kleiber, vice president of the French Academie des Sciences Philippe Taquet, Senate Speaker Bogdan Borusewicz and Deputy Minister of Science and Higher Education Zbigniew Marciniak. President Bronislaw Komorowski and the President of Warsaw Hanna Gronkiewicz-Waltz wrote letters to the participants. On behalf of French President Nicolas Sarkozy, the director of his cabinet Christian Fremont reminded that Maria Skłodowska-Curie was buried in the Paris Pantheon. "Many wives of prominent men rest there, but she was the first woman buried there in recognition of her own merits. She was also the first person from abroad, who was buried there" - he emphasised. The ceremony was also an occasion to officially put into circulation a collector banknote with denomination of PLN 20 with the image of Maria Skłodowska-Curie. Also presented were two Polish-Swedish post stamps "100 Years of Nobel Prize in chemistry for Maria Skłodowska-Curie".

(<http://www.naukawpolsce.pap.pl>, 15.12.2011)