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2,941,994

METHOD FOR THE PREPARATION OF HMX USING BORON TRIFLUORIDE

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5 Claims. (Cl. 260—239)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment to me of any royalties thereon.

The present invention relates to the preparation of high explosives of the nitramine type. More particularly the invention pertains to an improved method for the preparation of the explosive known as HMX, in good yield and purity.

HMX, variously known as homocyclonite, cyclotetramethylene tetranitramine, and 1, 3, 5, 7 tetranitro-1, 3, 5, 7 tetraazocyclooctane is known to be an explosive of great power and brisance. The detonation rate attainable with HMX strongly suggests the desirability of its use as a military explosive. Unfortunately known methods for the preparation of HMX from hexamethylenetetramine (hexamine) have proven to be unsatisfactory in that the yields obtained were well below the limits of practicality and the product obtained was of inferior quality. The best yields of HMX obtained by the prior art methods were of the order of 50–55% or less based on one mole of HMX per mole of hexamethylenetetramine. It will be apparent that the procedures disclosed in the prior art do not lend themselves readily to large scale production.

Accordingly, a primary object of this invention is the provision of a commercially feasible and more expeditious method of producing homocyclonite.

A further object of the invention is the provision of a method of preparing homocyclonite from hexamethylenetetramine in good yield and purity with the aid of a suitable catalyst.

Other objects and advantages of my invention will be apparent as the invention is hereinafter more particularly described.

I have now found that the foregoing objects may be accomplished by converting hexamethylenetetramine into HMX under mild nitrating conditions and in the presence of a catalyst such as boron trifluoride with or without the presence of a stabilizing agent such as formaldehyde. By means of the use of such stabilizing and catalytic agents it is possible to obtain a product containing 15–20% more HMX than is possible with prior art methods, thus resulting in a lowering of the cost of manufacturing HMX on large scale production. More specifically I have found that HMX is obtainable in a purity of 80–86% and an overall yield of 90–96% of theoretical based on the weight of hexamine when the hexamine is treated with nitric acid-ammonium nitrate mixtures of ratios varying from 15:14 to 15:12 in an acid medium consisting of a mixture of acetic anhydride and acetic acid. A small quantity of boron trifluoride (from 1 to 15% based on the weight of hexamine) is added to the reaction mixture as a catalyst. Optionally, a small quantity of formaldehyde (0.27 to 0.54 mole equivalent) may be added to the reaction mixture as a means of enhancing the conversion of hexamine to HMX.

Experimentation has indicated that the nitrating conditions must be mild in order to obtain good yields of

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HMX since under stronger conditions of nitration the main reaction product is RDX (cyclonite). It is for this purpose that mild nitrating conditions have been developed by using a large percentage of ammonium nitrate; by keeping the reaction mixture at relatively low temperatures (40–50° C.) and by using acetic acid as the nitrating medium.

The overall reaction involved in this invention may be represented as follows:

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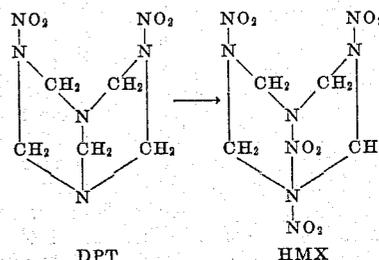
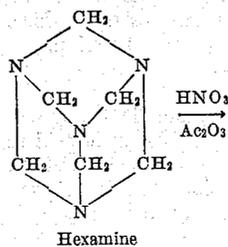
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The invention is more specifically illustrated by the following examples in which, as well as throughout the specification, all proportions are given in terms of weight unless specifically stated otherwise.

Example I

To a one liter flask, equipped with a stirrer, thermometer and three dropping funnels, were added 125 ml. of glacial acetic acid, 2 ml. of acetic anhydride and 1.6 grams of boron trifluoride. The temperature of the reaction mixture was maintained at $44 \pm 1^\circ \text{C}$. by means of a water bath. Over a fifteen minute period there was added with constant stirring a solution of 17 grams of hexamine dissolved in 28 grams of glacial acetic acid, 50 ml. acetic anhydride and 20 ml. of a nitric acid-ammonium nitrate solution via appropriate dropping funnels. The nitric acid-ammonium nitrate solution was prepared by dissolving ammonium nitrate in 98% nitric acid in the weight ratio of 15 to 14. This latter solution should be kept above 20°C . to prevent crystallization of the ammonium nitrate from solution. The hexamine and nitric acid solution were added continuously and proportionately over the fifteen minute period. At the end of each 3-minute period, 8 ml. of acetic anhydride were added to the reaction flask with the exception of the final addition which consisted of 18 ml. of acetic anhydride. The reaction mixture was then aged for about 15 minutes. After the aging period, 30 ml. of nitric acid-ammonium nitrate solution, prepared as above, and 30 ml. of acetic anhydride were added continuously and proportionately over a fifteen minute period, followed immediately by a 45 ml. addition of acetic anhydride. The reaction mixture was again allowed to age, this time for a period of approximately one hour. The reaction mixture was then refluxed with 700 ml. water for a period of thirty minutes, cooled to about 20°C . by the addition of ice, filtered, and the product washed with several portions of cold water and dried. The crude yield was 34.2 grams or 95% of theoretical. The purity of the material was approximately 80–83%.

Example II

The same procedure and the same ingredients as recited in Example I were employed under the same conditions. Instead of employing only boron trifluoride as a catalyst, however, a mixture consisting of 50% boron trifluoride and 50% paraformaldehyde was used. The crude yield obtained was in the order of 90-96% with a purity of 85-88%.

Although the role of the paraformaldehyde in the reaction is not fully understood, experimental evidence shows that the presence of the paraformaldehyde enhances the transformation of the intermediate product DPT into HMX. The formaldehyde may be added either continuously in gaseous form or added all at once in the form of paraformaldehyde at the beginning of the reaction.

Example III

The same procedure as found in Example I was employed with the exception that the ratio of nitric acid to ammonium nitrate was 15:12 on a weight basis and the total amount of nitric acid-ammonium nitrate solution used was 48.5 ml. The yield and purity was comparable to those of Example I.

The proportions of the various reactants recited in the above specific examples are not to be considered as limiting the scope of the process of this invention. The mole ratios of nitric acid and ammonium nitrate used to prepare the HMX may be varied from 5 to 7 moles and from 3 to 5 moles respectively per mole of hexamine. The acetic anhydride may be varied in mole ratio between 10 and 11 moles per mole of hexamine. The boron trifluoride may be added to the acetic acid-acetic anhydride solution in quantities of from 1 to 15% based on the weight of the hexamine and the formaldehyde in quantities of from 0.27 to 0.54 mole per mole of hexamine.

While the instant invention has been shown and described herein, in what is considered to be the most practical and preferred embodiments, it is to be recognized that departures may be made therefrom within the scope of the invention, which is therefore not to be limited to the details herein, but is to be accorded the full scope of the claims so as to embrace any and all equivalents.

What is claimed and desired to be secured by United States Letters Patent is:

- 1. In a process for the manufacture of homocyclonite wherein hexamine is converted to homocyclonite by treatment with nitric acid-ammonium nitrate solution in an acidic medium, the improvement consisting of carrying out the reaction in the presence of boron trifluoride as a catalyst.
- 2. A process for the manufacture of homocyclonite from hexamine as recited in claim 1 wherein said boron trifluoride is present in amounts ranging from 1 to 15% based on the weight of the hexamine.
- 3. The process of claim 1 wherein formaldehyde and paraformaldehyde is added to the reaction mixture as a stabilizing agent.
- 4. The process as recited in claim 1 wherein the temperature is within the range of from 40° to 50° C.
- 5. The process as recited in claim 1 wherein the acid medium comprises a mixture of acetic acid and acetic anhydride.

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