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2,983,725

METHOD FOR THE PREPARATION OF HMX

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6 Claims. (Cl. 260-239)

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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 and more particularly pertains to an improved method for the preparation of the explosive known as HMX, in good yield and purity without the necessity of isolating the intermediate product DPT (1,5-dinitroendomethylene-1,3,5,7-tetraazocyclooctane.

HMX, variously known as homocyclonite, cyclotetramethylenetetranitramine and 1,3,5,7-tetraazocyclooctane, is known to be an explosive of great power and brisance. The detonation rate attainable with HMX suggests the desirability of its use as a military explosive. Unfortunately, known methods for its preparation from hexamine (hexamethylenetetramine) have proven to be unsatisfactory in that the yields obtained were well below the limits of practicality; the product was of an inferior purity and it was necessary to isolate the intermediate product DPT.

The best yields of HMX obtained by prior art methods were of the order of 50-55% or less based on one mole of HMX per mole of hexamethylenetetramine. It will therefore be apparent that procedures disclosed in the prior art do not lend themselves readily to the large scale manufacture of HMX.

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, without necessitating the isolation of the intermediate product DPT and which is directly applicable to large scale production.

Other objects and advantages 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 stabilizing agent such as formaldehyde. More specifically, I have found that HMX is obtained in 90-95% purity and 85% overall yield based on the weight of hexamethylenetetramine used when the hexamethylene is treated with nitric acid-ammonium nitrate mixtures of ratios varying from 15:8 to 15:15, in an acid medium consisting of a mixture of acetic anhydride and acetic acid. A small quantity of formaldehyde (0.27-0.54 mole equivalents) must be added to the reaction mixture and the temperature of the reaction maintained at between 40-48° C. by means of external cooling.

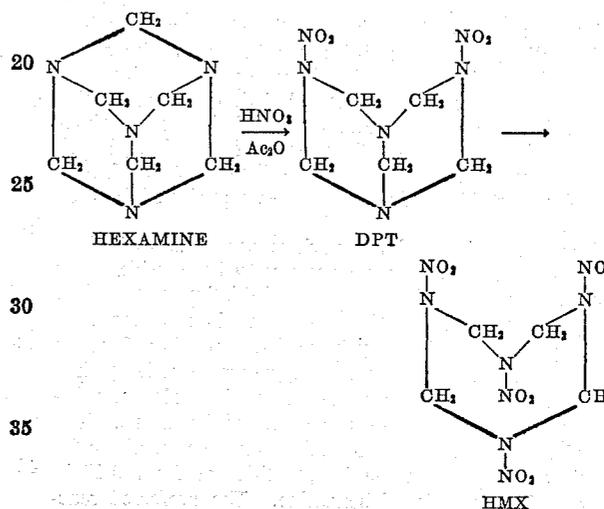
Experimentation has indicated that the nitrating conditions must be mild in order to obtain good yields of HMX since under stronger conditions of nitration the main reaction product is RDX (cyclonite). It is for this purpose that mild nitrating conditions have been developed by using a large ratio of ammonium nitrate;

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by keeping the reaction mixture at rather low temperatures, and by using acetic acid as the nitrating medium.

The formaldehyde is added to the reaction mixture as a means of stabilizing the principal intermediate, DPT, and to enhance the transformation of DPT into HMX. Although the role of the formaldehyde in the reaction is not fully understood, experimental evidence indicates that the presence of formaldehyde markedly increases the conversion of hexamethylenetetramine to HMX. The formaldehyde may be added either continuously in gaseous form or all at once in the form of paraformaldehyde at the beginning of the reaction. The type of paraformaldehyde used is of importance to the extent that better results have been obtained with material melting below 125° C. than above that temperature.

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



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

785 grams glacial acetic acid, 13 grams acetic anhydride and 17 grams of paraformaldehyde were added to a suitable flask (6 to 10 liters) equipped with stirrer, thermometer and three dropping funnels. The temperature of the reaction was maintained at 44±1° C. by means of a water bath. 320 grams acetic anhydride, 180 grams nitric acid-ammonium nitrate solution and a solution of 101 grams hexamine dissolved in 165 grams acetic acid were then added to the reaction mixture via dropping funnels over a period of 15 minutes with constant stirring of the reaction mixture. The nitric acid-ammonium nitrate solution was prepared by dissolving 233 grams ammonium nitrate in 218 grams of nitric acid (99% or better). This latter solution should be kept above 20° C. to prevent crystallization of ammonium nitrate from solution.

The hexamine and nitric acid solutions were added continuously and proportionately. After the addition of 66.5 grams of the hexamine solution, 64 grams of the acetic anhydride were added in bulk. A similar amount of the anhydride was added after the addition of each 66.5 grams of the hexamine solution except that after all the hexamine had been added a final addition of 128 grams of acetic anhydride was made to bring the total up to 320 grams. After the addition of the above ingredients, the reaction mixture was aged for approximately 15 minutes. After the aging period, 480 grams acetic anhydride and 271 grams nitric acid-ammonium nitrate solution were added over a fifteen minute period in the following manner; 320 grams acetic anhydride and 271

grams nitric acid-ammonium nitrate solution were added continuously and proportionally and then 160 grams acetic anhydride in bulk. The reaction mixture was again allowed to age, this time for a period of about one hour.

After aging, purification of the product may be accomplished by the addition of hot water and refluxing the mixture for about an hour. In this instance the mixture was poured into a 7-10 liter flask equipped with a suitable reflux condenser. 350 grams of hot water (75-90° C.) were added to the flask and the reaction mixture heated at reflux for 30 minutes. The reaction mixture was then cooled to about 20° C. by means of an ice bath and the addition of approximately 2000 grams of ice to the mixture. The resulting water insoluble material was filtered out and washed with three portions of cold water amounting to about 400 grams each. The product was then dried. The crude yield was approximately 200 grams or 95% of theoretical. The purity of the product was better than 90% HMX, the residue being largely RDX.

The product obtained through the above process is a white solid having crystal-like needles and is the alpha form of HMX. The alpha form may be easily converted to the beta form by crystallization from a hot solvent solution such as acetone, acetonitrile or cyclohexanone using equal parts by weight of the alpha HMX and the solvent. The resulting white crystals of beta HMX melt at 278-279° C. and have a purity of 99% or better.

The proportions of the various reactants recited in the above specific example 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 paraformaldehyde may be added to the acetic acid-acetic anhydride solution in quantities of from 0.27 to 0.54 mole per mole of hexamine. The preferred reaction temperature ranges between 40 and 48° C.

While the instant invention has been shown and described herein, in what is conceived to be the most practical and preferred embodiment, 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. A process for the manufacture of homocyclonite which comprises reacting hexamine in an acetic acid-acetic anhydride medium with (1) nitric acid which is present in the ratio of from about 5 to 7 moles per mole of hexamine and (2) ammonium nitrate which is present in the ratio of from about 3 to 5 moles per mole of hexamine and (3) from about .27 to .54 mole per mole of hexamine of a stabilizing agent selected from the group consisting of formaldehyde and paraformaldehyde.

2. The process according to claim 1 wherein the reaction temperature is maintained between 40° and 48° C.

3. The process according to claim 1 wherein the acetic anhydride is present within the ratio of from about 10 to 11 moles per mole of hexamine.

4. The process according to claim 1 wherein formaldehyde is added in the gaseous state.

5. A process for the manufacture of homocyclonite which comprises reacting hexamine in an acetic acid-acetic anhydride medium with a nitric acid-ammonium nitrate solution, said solution having a mole ratio of from about 15:8 to 15:15, and from about .27 to .54 mole per mole of hexamine of a stabilizing agent selected from the group consisting of formaldehyde and paraformaldehyde.

6. The process according to claim 5 wherein the reaction temperature is maintained between 40° and 48° C.

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