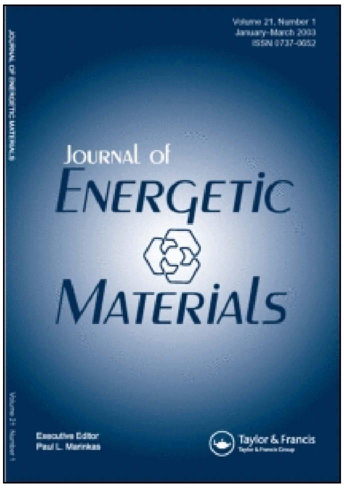

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Comparative Study on the Role of DPT on the Formation of HMX in Semi-Batch and Continuous Process

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3,7-Dinitro-1,3,5,7-tetrazabicyclo-[3,3,1]nonane (DPT) is a key intermediate in the preparation of octahydro-1,3,5,7-tetranitro 1,3,5,7-tetrazocine (HMX), one of the most powerful high-melting explosives. The present investigation focuses on DPT formation during semi-batch and continuous processes. Qualitative and quantitative picture has been brought out to realize the role of DPT in HMX formation. The study reveals that only two thirds of DPT is formed in the continuous process as compared to that of semi-batch process. The calculated final yield of HMX on reaching steady state in the continuous process is comparable to the semi-batch process. This study also illustrates the usefulness in understanding the role of DPT in the final yield of HMX.

Keywords: chemical processes, chemical reactors, DPT, HMX, scale-up

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Introduction

HMX is the most powerful explosive manufactured in bulk at present. HMX finds potential applications in shaped charges, plastic-bonded explosives, and nitramine-based propellants. It is manufactured by modified Bachmann synthetic route [1,2] and the synthesis involves complex series and parallel reactions. Some of the important intermediate/side products obtained in its synthesis are 3,7-dinitro-1,3,5,7-tetrazabicyclo-[3,3,1]nonane (DPT), hexahydro-1,3,5-trinitro 1,3,5,-triazine (RDX), 1-acetoxy-methyl-3,5,7-trinitro-1,3,5,7-tetraza cyclooctane (PHX), 1,7-di-acetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX), 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraza nonane (AcAn), etc. [3,4]. Nitrolysis of hexamine under mild acidic and low-temperature conditions yields DPT in the initial stages [5]. This DPT on further nitrolysis is converted to HMX (Fig. 1). Thus, DPT formation is very important as a precursor to HMX and determines the overall yield of HMX. Hence, a systematic study has been carried out in both semi-batch and continuous modes of operation for understanding the formation of DPT.

Product distribution in a chemical reaction depends on contacting patterns in various reactors [6]. In the present study, HMX synthesis is carried out by semi-batch as well as continuous processes. A batch process is used to produce a comparatively small amount of material or to produce many different products from one piece of equipment [7]. On the other hand, for the chemical treatment of materials in large quantities, a continuous process is more economical and safer. Product quality is uniform in continuous processing. Processing of explosives

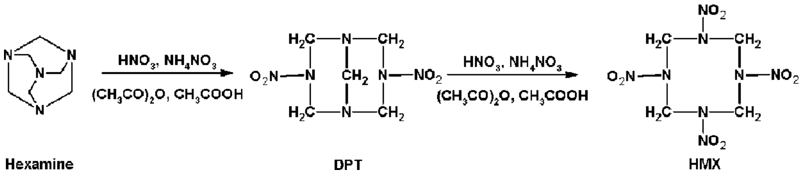

Figure 1. Nitration of hexamine.

by continuous stirred tank reactor (CSTR) is safe due to handling of less explosive at any instance in the reactor.

Process analytical chemistry (PAC) information may be used to control and optimize the performance of a chemical process in terms of capacity, quality, cost, consistency, and waste reduction [8–10]. PAC may be implemented through off-line, at-line, and on-line analysis. Since the present investigation focuses on the formation of DPT and HMX, PAC is implemented through at-line analysis to monitor the process parameters. A high-performance liquid chromatographic (HPLC) study has been carried out to identify the products that are formed during various stages of CSTR.

Experimental

HMX is synthesized from hexamine in two stages of nitration using nitric acid–ammonium nitrate as nitrating agent in acetic acid and acetic anhydride medium. In order to ensure the completion of reaction, sufficient time (aging) is given after both stages of nitration. The complete synthesis can be executed by both semi-batch and continuous processes. The details of the process are described below.

Semi-Batch Process

Three hundred seventy milliliters of acetic acid, 15 mL of acetic anhydride, and 8.5 g of paraformaldehyde were taken in a 2-L RB flask fitted with a stirrer assembly. Solution A, consisting of 50 g of hexamine dissolved in 80 mL of glacial acetic acid, and solution B, consisting of 43 g of ammonium nitrate dissolved in 31 ml of 98% nitric acid, were prepared. Solution A, Solution B, and 120 mL of acetic anhydride were added to reaction mixture for 30 min during the first stage and the temperature was maintained at 44 ± 2°C. After the first stage of nitration, the reaction mixture was uniformly stirred at the same temperature (aging stage 1).

Nitric acid–ammonium nitrate solution was prepared by dissolving 64.8 g of ammonium nitrate in 48 mL 98% nitric acid. In the second stage of nitration, nitric acid–ammonium nitrate solution and 215 mL acetic anhydride were added to the reaction mass for 30 min and then it was stirred for an hour at 44°C (aging stage 2). Finally, 500 mL of water was added to the reaction mass and the temperature was raised to 98°C. The whole mass was kept at this temperature for 30 min and then it was allowed to cool at room temperature. The mixture was filtered and the solid was washed repeatedly with water and subsequently was dried.

Samples were taken from the reaction mixture at regular intervals during first aging stage. Concentration of DPT formed during the first stage aging was monitored periodically.

Continuous Process

Continuous process was studied by using four continuous stirred tank reactors in series. CSTRs were designed to process 1 kg of hexamine per hour. The schematic diagram of the continuous process is shown in Figure 2. The process was carried out for 4 h. Solutions A and B were prepared by dissolving 4 kg of hexamine in 36 L of acetic acid and 8.6 kg of ammonium nitrate in 6.4 L of 98% nitric acid, respectively. Solutions A, B, and 29.5 L of acetic anhydride were added continuously for 4 h. Eighty-five grams of paraformaldehyde was added to the N_1 at regular intervals of 30 min. Nitration reactions were carried out in two stages in the first (N_1) and third (N_2) reactors, while the aging of the reaction mass was carried out in the second (A_1) and fourth (A_2) reactors. The average residence time of reactors 1 and 2 were 45 min each and reactor 3 was 30 min. In the first CSTR, complete solution of A, 40% of solution B, and 40% of acetic anhydride were added using the precalibrated peristaltic pumps. The remaining portion of solution B and acetic anhydride were added in N_2.

After 4 h of nitration, reaction mass was diluted with equal amount of water and heated to 98°C. This process is called simmering, where the linear chain nitro compounds are disintegrated into smaller molecules. After simmering,

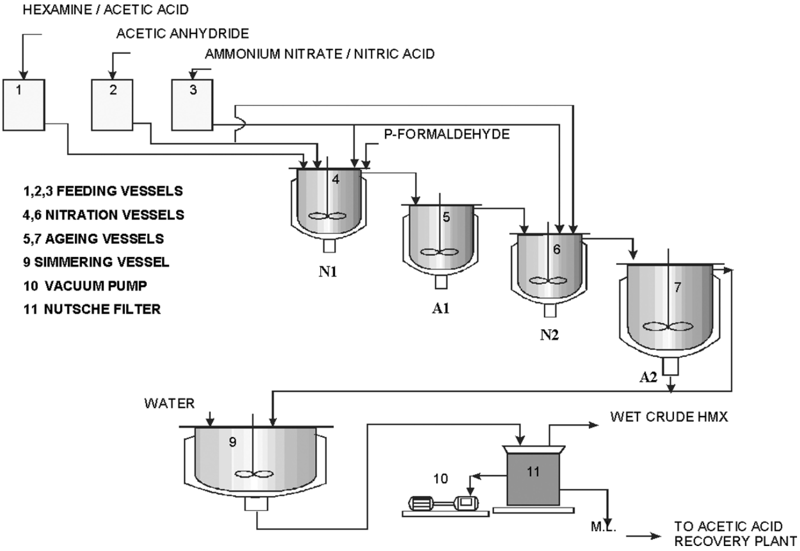

Figure 2. Schematic diagram for continuous processing of HMX in CSTR battery.

the reaction mass was cooled. The product was filtered, dried, and weighed.

Samples were withdrawn at regular interval of 30 min and the density at 44°C was calculated by weighing known volume of reaction mass. Water was added to quench the reaction and the solids were filtered off to determine the solid concentration. Particle size analysis of the representative samples in each CSTR was carried out using Malvern particle size analyzer. Temperatures in all four vessels were recorded during the process. Chromatographic analyses were carried out in a Waters Alliance HPLC system equipped with auto sampler and UV-visible absorbance detector. Isocratic elution was performed using 3.9×150 mm Novapak C_{18} (4 μm) column with the mixture of acetonitrile, methanol, and water (5:35:60) as an eluent. The total injection volume was 10 μL and the detection wavelength was 254 nm. Acetonitrile was used for the sample preparation.

Results and Discussion

Semi-Batch Process

It is reported that the material isolated during aging is mainly DPT and the present study confirms the same [11,12]. DPT was observed to decompose at 191°C. The compound was uniform in all the isolated samples during aging stage 1. This shows that the material formed during the aging time of nitrolysis of hexamine was the same throughout the experiment and no other side reactions take place at this stage.

The plot of aging time versus amount of isolated material is shown in Figure 3. The graph shows that the quantity of material increases exponentially with aging time and the trend is similar in both cases (with and without paraformaldehyde). With paraformaldehyde, the maximum quantity of isolated material was obtained in 15 min, whereas it was 25 min without paraformaldehyde. Castorina et al. [11] revealed that when paraformaldehyde is included in the nitrolysis medium, its methylene groups can enter it into a common pool with those

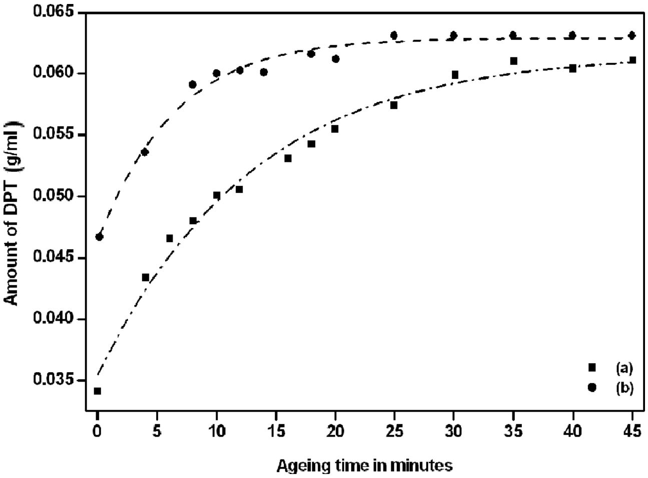

Figure 3. Plot of aging time versus amount of isolated material in semi-batch process. (a) Without addition of paraformaldehyde; (b) with addition of paraformaldehyde.

from hexamine for the formation of final products. The present study reveals that the enhancement in formation of DPT is resulted by using the reaction aid paraformaldehyde.

In order to achieve the maximum yield in any chemical reaction, it is necessary to understand the reaction kinetics, which will be useful in designing the reactor. In the present investigation, the obtained data were analyzed to understand the reaction kinetics of DPT formation during aging. The obtained data are fitted to first-order rate equation for both with and without paraformaldehyde cases. Figure 4 shows that the best fit is obtained by plotting concentration versus time (t), which gives a straight line passing through the origin. The slope of this line gives the first-order rate constant. The rate constants are found to be 0.11 min^{-1} with paraformaldehyde and 0.08 min^{-1} without paraformaldehyde. But a poor fit was observed in the case of zero- and second-order rate equations. Hence, this indicates that the formation of DPT during aging follows first-order kinetics.

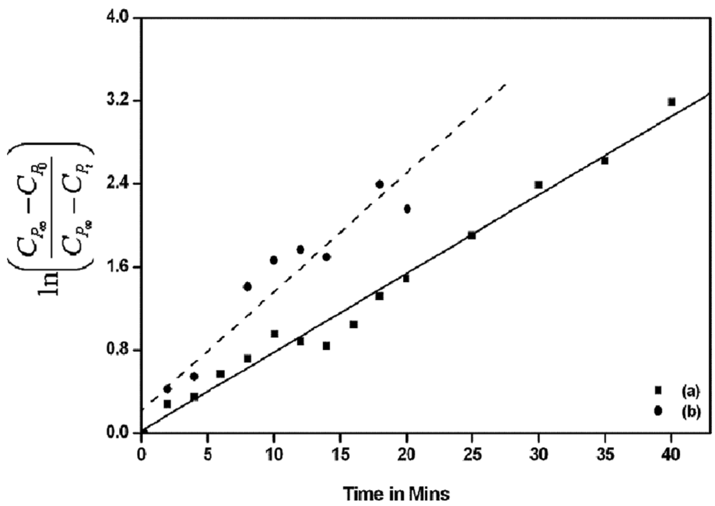

Figure 4. Verification of first-order rate equation for the formation DPT during aging. (a) Without addition of paraformaldehyde; (b) with the addition of paraformaldehyde.

Bachmann et al. [5] prepared DPT by the nitrolysis of hexamine with the yield of about 48% and on further nitrolysis of DPT, they obtained 75% of crude HMX based on DPT. The maximum yield of about 65% DPT was obtained by the Castorina et al. [11] by quenching the product of nitrolysis of hexamine after aging stage 1. In the present study, nitration of hexamine yielded 72% DPT (hexamine basis), which on further nitration gave 82% HMX (DPT basis). The overall yield of HMX was about 60%. The highly acidic reaction media restricts the complete analysis of reaction mixture.

Continuous Process

Reaction temperature plays a vital role in deciding the product purity, yield, and selectivity, especially in series/parallel reactions. In the present study, the temperature of the CSTR batteries was recorded at regular intervals. The temperature in CSTRs 1, 2, and 3 reached 44°C due to exothermicity of the reaction. The time required to achieve 44°C in the above reactors was found to be 25, 75, and 35 min, respectively. Since there was no addition of reactants in A_1, the temperature rise was observed to be slow. A_2 did not attain the required temperature of 44°C, due to the large vessel size and no addition of reactants. The required temperature can be achieved by heating the vessel with hot water circulation through the jacket.

The qualitative information about the nature of the product and the behavior of reaction fluid can be obtained from the density of the reaction mass. In the present study, density of the medium was measured at an interval of 30 min and the results are shown in Figure 5. N_1 and A_1 lines show that the density attains maximum after 2 h and remains constant. This result suggests that a minimum time of 2 h is required to reach steady-state for DPT formation. Higher density in N_1 compared to that of A_1 may be attributed to the continuous addition of reagents having higher density (density of solution $B = 1600\,kg/m^3$) in N_1. In contrast, N_2 shows different behavior compared to others. This reveals that the nature of the product

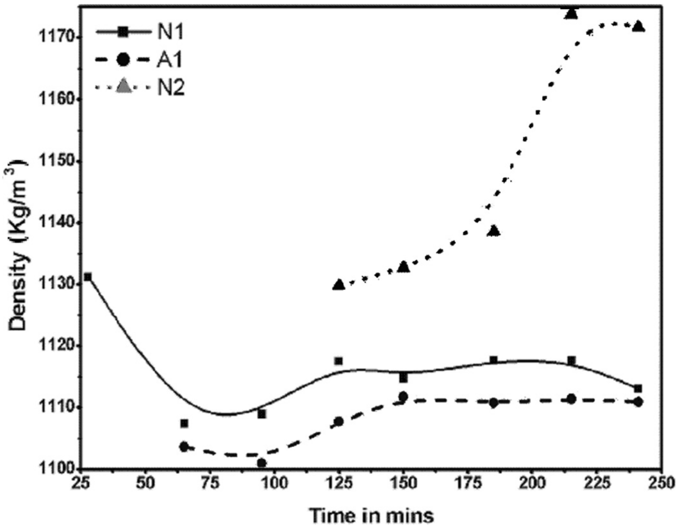

Figure 5. Density profile in CSTRs.

formed itself is different from N_1 and A_1. Further, the N_2 trend line shows that about 3 h is needed to reach steady-state. Hence, a minimum of 3 h is required to reach overall steady-state from the beginning.

Solid content in the reaction mass gives a direct estimate of the product formation. DPT formation in N_1 and A_1 was increased up to 2 h and beyond that it reached steady-state as shown in Figure 6. In contrast, the product formation at N_2 takes 3 h to attain steady-state. This follows the same trend exhibited in the density profile of the reaction medium. Solid concentration in N_2 shows that there is a formation of new material whose concentration is 0.1 g/mL against 0.04 g/mL of DPT at steady-state (N_1 and A_1 stages).

In the continuous process, the overall yield of HMX was about 45%, in contrast to 60% in semi-batch process. However, the yield calculated after reaching steady-state was about 63%. Particle size was determined for the isolated solid product by using Malvern particle size analyzer. Surface-weighted mean diameter of the samples in N_1 and A_1 were nearly the same

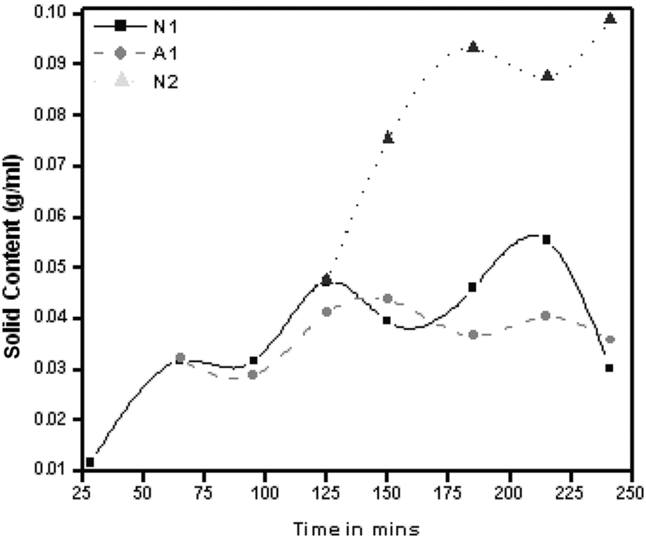

Figure 6. Solid content profile in CSTRs.

(21 and 23 µm), whereas particle size of the material isolated from N_2 was 2 µm. The final HMX obtained after simmering was found to be 3 µm. Since DPT is present in N_1 and N_2, the observed particle size was similar. During the second nitration, the particle size was drastically reduced. In N_2, a heterogeneous reaction takes place between the solid DPT and the remaining reactants in liquid phase. As a result, the size of the DPT core may shrink with time due to the surface reaction and result in the new product with smaller particle size.

Composition of the isolated product in representative samples is analyzed by using high-performance liquid chromatography (HPLC) studies. Crude HMX obtained after simmering and filtration contains 72% of HMX and 27% of RDX. This reveals the absence of linear chain nitro compounds after simmering.

HPLC is a powerful tool in exploring reaction paths as well as in understanding the reaction mechanisms. In the present investigation, the HPLC study revealed the presence of DPT in the isolated solids at N_1 and A_1 stages and there is no formation of RDX or HMX in the N_1 and A_1 stages. In continuous process, in order to achieve better insight of the process parameters, the samples were withdrawn from the N_1, A_1, and N_2 CSTR batteries after 3 h of reaction. The samples were analyzed using HPLC and the chromatograms are shown in Figure 7. Similar to semi-batch process results, the formation of only DPT is identified at N_1 and A_1 stages and no significant amount of DPT is identified in the N_2 reactor. Only the mixture of RDX and HMX are observed in the case of the N_2 sample as well as in the final crude HMX. This study clearly showed that no formation of RDX occurred during N_1 and A_1 stages. Further, the product purity of final HMX can be improved by focusing on the N_2 stage reaction control rather than N_1 and A_1.

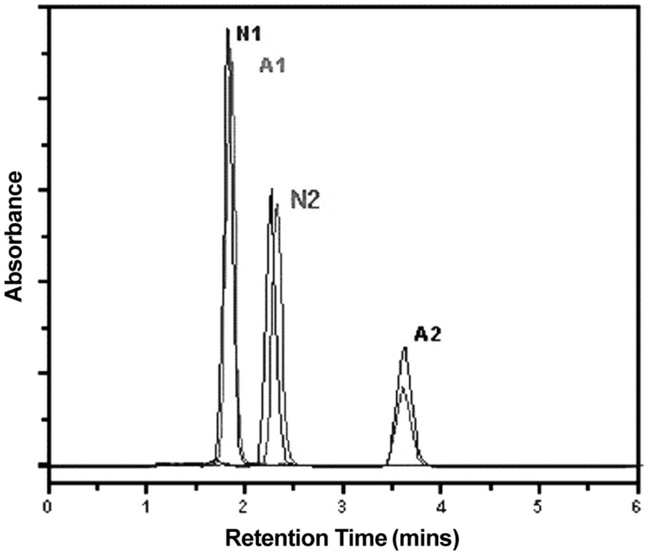

Figure 7. Chromatograms of the isolated solids from different CSTRs after 3 h of continuous process. (In N_1 and A_1, HPLC confirms the presence of only DPT; in N_2 and A_2, HPLC confirms presence of mixture of HMX and RDX.)

Comparison of Semi-Batch versus Continuous Process

In the case of semi-batch process, DPT formation takes about 15 min to reach maximum of 0.06 g/mL of solid content during aging stage 1, while in continuous process, maximum solid content of 0.04 g/mL was obtained after 85 min of aging stage 1. Overall amount of DPT formed in continuous process at steady-state was two thirds of semi-batch process. This behavior was reflected in the final yield of HMX, which was about 45% for continuous process in contrast to 60% in semi-batch process. The delay in achieving steady-state may be attributed to improper residence times realized by the molecules. Further, DPT decomposes on prolonged exposure in the acidic reaction medium [11]. Hence, continuous process for the preparation of HMX gives overall less yield. However, the yield is comparable to semi-batch process if the yield is calculated after reaching steady-state. This study reveals that in order to improve the productivity, the process may be conducted for a longer duration.

Conclusions

Studies on the formation of DPT during aging show that the reaction follows the first-order kinetics. Paraformaldehyde addition increases the DPT formation. Only two thirds of DPT is formed in continuous process compared to that of semi-batch process. The calculated final yield of HMX after reaching steady-state in the continuous process is comparable to semi-batch mode. Chromatographic investigations clearly revealed that there is no formation of RDX during N_1 and A_1 stages and the product purity can be improved by the careful reaction control at the N_2 stage to minimize the RDX content. Hence, the study finds its usefulness in understanding the role of DPT on the formation of HMX.

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