Follow-up and Kinetic Model Selection Of Dinitro Pentamethylene Tetramine (DPT)

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Abstract: The Synthetic route of Cyclotetramethylene Tetramine is implemented through the reaction of hexamine and nitrating mixture that is formed as a result of a reaction between ammonium nitrate and fuming nitric acid. The reaction medium includes acetic acid, acetic anhydride and p-formaldehyde. This synthetic pathway is relatively long and both of hexamine dinitrate and Dinitro Pentamethylene Tetramine (DPT) are considered as the two main intermediate compounds. The former compound (hexamine dinitrate) was prepared, purified, and then characterized. Conversion of hexamine dinitrate into DPT has been followed up experimentally at different temperatures. Various factors including temperature and time has been investigated. The obtained results were reliable and consistent with the literature. Different kinetic models have been tested. The unreacted core model proved to be applicable and the surface reaction was found to be controlling.

Index Terms: Energetic materials, DPT, Characterization, Analysis techniques, Synthesis, Nitramines, RDX, HMX.

I. INTRODUCTION

Energetic materials have been widely used for several civilian and military applications. The design of reliable defense systems requires energetic material formulations with high performance and low vulnerability. So, there are several design considerations should be taken into consideration for such formulations including not only improved mechanical properties, extended service life and reduced environmental impact in manufacture, but also use and disposal [1].

Bachmann and Sheehan [2] developed a protocol of preparing DPT. This protocol adopted the nitrolysis of hexamine using ammonium nitrate – nitric acid solution and acetic anhydride. Hexamine Dinitrate is considered as an important starting material in the process of DPT production, while Hexogen (RDX) and Octogen (HMX) are also considered as a source of the methylene base and the simultaneously bound "anhydrous" nitric acid in an advantageous crystalline and relatively stable form [3-6].

HMX is one of the most powerful military explosive; however it has a limited use as a result of its high cost. It was reported that HMX could be manufactured nitration of hexamine. HMX can also be prepared from DPT, which has been recognized as a key intermediate in the formation of HMX from the nitration of hexamine in a process called modified Bachmann process.

The direct nitrolysis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1] nonane (DPT) is a feasible and reliable way to synthesize HMX as it has multiple practical applications. There is also a new nitrolysis process involving the use of an N_2O_5-HNO_3 system catalyzed by acidic ionic liquids (AILs) [7]. Moreover, the effect of metallic ions on the nitrolysis of DAPT [3,7-diacetyl-1,3,5,7-tetraazabicyclo(3.3.1) nonane] and HA (hexamine) was investigated by experimental and theoretical approaches [8].

II. EXPERIMENTAL WORK

2.1 Raw Materials and Instrumental Analysis

All samples were prepared and filtered in a special fuming hood equipped with glass shelter and a powerful air suction system for ventilation. Safety regulations have been strictly applied due to the nature of the used materials. To handle these kinds of energetic materials, best safety practices (leather gloves, face shield) are strongly recommended.

2.2 Synthesis of DPT from Hexamine Dinitrate

Hexamethylene Dinitrate ("Hexamine" Dinitrate) is an important intermediate in the pathway of preparation of DPT (Dinitro–Pentamethylene-Tetramine). It is prepared [9,10] through the addition of a solution of Hexamine (10g, 0.07mol) in distilled water (17.5ml, 0.972mol) drop by drop to nitric acid (specific gravity =1.4, 11.75ml, 0.261mol) already present in the above-mentioned setup. The reaction temperature was fixed at 15˚C; and the rate of addition of Hexamine solution was controlled to meet this condition. Finally, the mixture was cooled to 5˚C and Hexamine Dinitrate was separated from the reaction mixture using a vacuum pump and dried in a vacuum oven.DPT was also prepared starting from the hexamine dinitrate. To a mixture formed of glacial acetic acid (5ml, 0.0874mol) and acetic anhydride (2ml, 0.0212mol), hexamine dinitrate (1g, 0.00375mol) was added as one portion. Then the reaction mixture was left, for a fifteen minute period, at a temperature of (44 ± 1˚C) which was also maintained throughout this procedure.

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The reaction mixture was then quenched by chilling it to 12˚C. Rapid separation of the solid phase was then carried out.

2.3 Synthesis of Octogen (HMX)

HMX was prepared starting from hexamine according to the procedure described by Fedoroff and Sheffield [11]. This method involved the introduction of glacial acetic acid (26.16g, 0.436mol), acetic anhydride (0.433g, 0.00425mol) and p- formaldehyde (0.566g, 0.01887mol) into the above-mentioned reaction flask, keeping the temperature at 44 ± 1 °C. Over a fifteen minute period, a solution of hexamine (3.366g, 0.024mol) in glacial acetic acid (5.5g, 0.0916mol), acetic anhydride (10.66g, 0.1045mol) and a solution of ammonium nitrate in nitric acid prepared by dissolving ammonium nitrate (28g, 0.3498mol) in nitric acid (99% concentration) (30g, o.4762mol) were added simultaneously. These solutions were added continuously in correct proportions. The mixture was stirred for an additional fifteen minutes. Then, two reagents were then added in correct portions; acetic anhydride (10.667g, 0.1045mol) and nitric acid – ammonium nitrate nitrating solution (9.033g). Acetic anhydride (5.33g, 0.0523 mol) was then added as one portion. The mixture was then stirred for 60 minutes; hot water (11.6g, 0.648mol) was added. The reaction mixture was then refluxed for 30 minutes. The mixture was then cooled to 20°C. The solid phase was then separated and washed by cold water in a vacuum filter. The product was then dried in a vacuum oven.

2.4 Following up the conversion and the yield of Hexamine Dinitrate into DPT

DPT was prepared starting from Hexamine Dinitrate at different temperatures. At each temperature, the reaction was quenched by chilling it suddenly to 12°C. Quenching was followed by rapid filtration. The product was then washed and dried. Concentrations of both the unreacted Hexamine Dinitrate and the formed DPT were measured using the Agilent 1100 series HPLC. The effects of temperature and time were investigated. Reaction temperature was varied from 15 to 65°C; also reaction time was varied from 0 to 10 hrs.

Conversion of Hexamine Dinitrate into DPT was initially followed up from zero to 15 minutes at 45°C. This temperature has been recommended by two different authors [11- 15].Lower and higher temperatures have been also fixed during investigating the mentioned reactions. Results of the previously mentioned follow up are tabulated in tables (1-6). High performance liquid chromatography (HPLC) technique can be used as a qualitative and quantitative method of identification of energetic materials and other organic substances through the retention time and the peak area. HPLC can also be employed not only for separation purposes but also for identification, by comparing the retention time of the unknown compound to that of a known one (standard) under the same operating conditions. The instrument in this work was Agilent 1100 series HPLC instrument.

The column was Zorbax elipse (XDB-C8, analytical 4.6x150mm, 5-micron) the working temperature was 28˚C. The mobile phase was 30 % Acetonitrile (ACN) – 70 % water (HPLC grade). The UV detector was tuned at 220 nm. The flow rate was 0.5 ml/min., cover a period of 25 minutes, and the injection volume was 3 ml. Many experimental trials have been made in order to obtain chromatograms separated with high resolution. The mentioned operating conditions were used and separation was done perfectly.

III. RESULTS AND DISCUSSION

3.1 Calculating the yield of prepared compounds

Starting by 10 g of Hexamine; about 17 g of dry Hexamine Dinitrate was obtained. The average yield was therefore about 89 %. The yield; according to the published data is about 95 % [13]. Solubility of small fraction of the product in the spent acid may be the main cause of the recorded disagreement. Yield of the prepared DPT was about 65 % but in absence of Paraformaldehyde it was only about 30 %. These results are in good agreement with those found in the literature [2]. The prepared Hexamine Dinitrate was also converted into DPT under the action of Acetic Anhydride - Acetic acid mixture at about 45 ^{o}C according to the published procedures [2], [14]. After applying an aging process to the mixture for 15 minutes, it should be cooled down to about 12 ^{o}C by adding a suitable quantity of ice. The product was then filtered and dried under vacuum. Once more the yield was about 65%. Starting from Hexamine, proceeding towards the DPT- without separating it- and after adding an additional quantity of the nitrating mixture, aging for 15 minutes, refluxing on an oil bath at 130 ^{o}C, adding a suitable quantity of ice, the HMX crystals were separated, filtered and then dried. About 1.5g of the crude HMX was obtained per gram of the used hexamine. Characteristics of the dry product have been determined and Yield of the HMX is therefore 69.5 %.

At each temperature, the analysis was done at different reaction times. The above – mentioned figure shows the chromatogram obtained at the end of the investigated reaction time at 45°C. By examining the obtained chromatograms, the prepared compounds were identified and quantified. Concentrations of both unreacted and formed species were determined, where C_{A_o} and C_A are the initial and final concentrations of hexamine dinitrate respectively. The complete data and calculated results of HPLC analysis are summarized in Table 1.

Table (1) Calculated results of hexamine dinitrate conversion at different reaction times at 45°C.

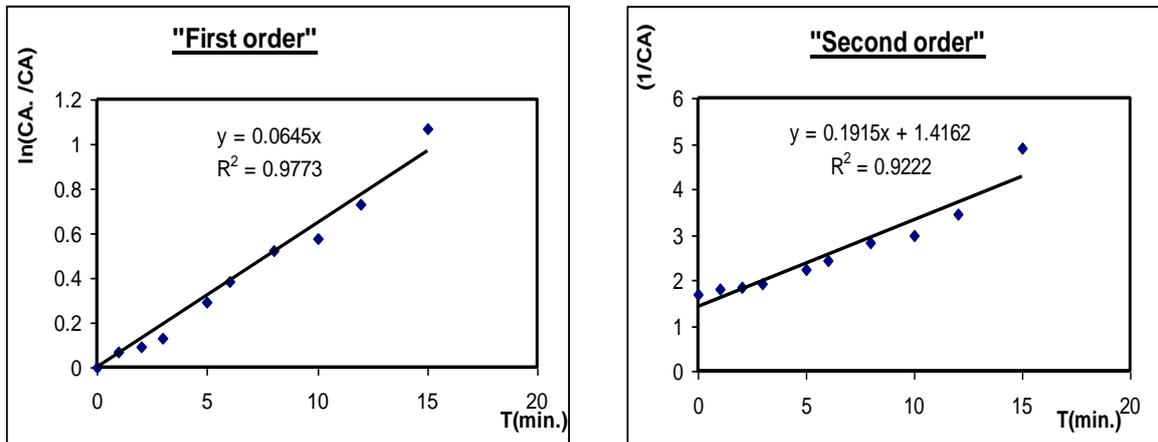| Time (min)	0	1	2	3	5	6	8	10	12	15
Hexamine dinitrate (mg/ml)	0.598	0.560	0.546	0.524	0.446	0.408	0.353	0.336	0.289	0.205
DPT (mg/ml)	0	0.0254	0.038	0.059	0.125	0.149	0.196	0.205	0.253	0.322
$\ln(C_{A_\circ}/C_A)$	0	0.0658	0.0904	0.132	0.294	0.382	0.527	0.577	0.728	1.072
$1/C_A$	1.672	1.785	1.830	1.907	2.244	2.449	2.831	2.977	3.461	4.884

**Fig. 1 Representation of the hexamine dinitrate concentration – time data
at 45 °C, according to first and second order kinetic models.**

As a first approximation, the reaction may be treated as a homogeneous one. From the concentration results, namely $\ln(C_{A_\circ}/C_A)$ and $(1/C_A)$, shown above, the rate constant was calculated for first and second order kinetic models respectively as shown in the following Figure 1. The obtained values of rate constant are summarized in Table 2.

From Table 2, it is clear that the calculated rate constant, according to the first order model, is nearly doubled for each decade of temperature rise up to 35 °C. However, at 45°C the rate constant increases almost sixteen times. Further increase of temperature, nearly 55°C and 65°C, has a slight effect on the rate constant. The results confirm the reported data in literature [11] that the optimal reaction temperature is 45°C. On the other hand, for the second order kinetic model, the increase of the rate constant with temperature is irregular and unjustifiable, especially at low temperatures. Moreover, the correlation factor values for the second order are inferior to those obtained for first order kinetic model. Arrhenius equation was used to calculate the activation energy of the reaction under investigation. The relation between ln(k) and (1/T) for both first and second order kinetic model is shown in Figures 2 and 3.
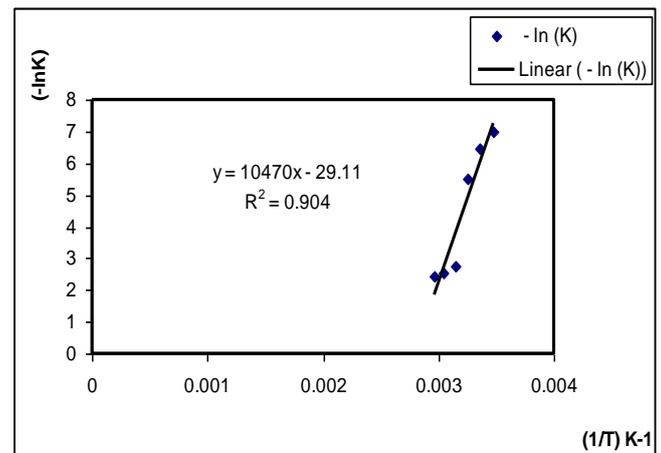

Fig. 2 Activation energy for the conversion of hexamine dinitrate into DPT according to the first order model.

The values of (E/R) are 10470 K and 11573 K and accordingly the activation energy is 87.05 kJ/mole and 96.22 kJ/mole for first and second order kinetic models successively.
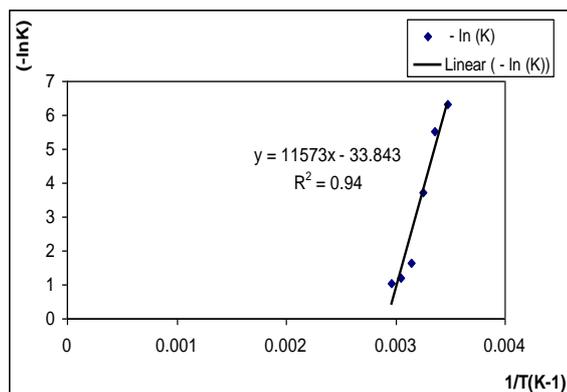
Fig. 3 Activation energy for the conversion of hexamine dinitrate into DPT according to the second order model.

IV. CONCLUSION

The work reports the synthesis of DPT as an important and key intermediate for the synthesis of RDX and HMX. Recently, new research efforts have been devoted to increase the performance of energetic materials using nanocomposites and nanoparticles due to its unique properties not only in the field of energetic materials but also in other applications including medical, environmental, and industrial applications. [16-41]

The yield of the DPT prepared was about 65%; while the yield of the hexamine dinitrate prepared was about 89%. The analysis of the prepared samples using an efficient HPLC was a very reliable procedure. Decomposition of hexamine dinitrate became faster than that found below this temperature. About two thirds of the hexamine dinitrate were depleted during the first fifteen minutes.

This temperature has been already recommended by many authors. The temperature of 45 ± 2 °C is the optimum temperature that gives the optimum conversion and yield. The analysis of the prepared samples using an efficient HPLC was a very reliable procedure. The concentrations and concentration terms found at 45°C were not fitting tightly to the ordinary second order kinetic model. Decomposition of hexamine dinitrate became faster and faster than that found below this temperature. About two thirds of the hexamine dinitrate were depleted during the first fifteen minutes. This temperature has been already recommended by many authors [6,10]. The applicability of the first order model which gave higher correlation coefficient when compared with the second.

ACKNOWLEDGMENT

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