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Coversion of Hexamine Dinitrate into Dinitro Pentamethylene Tetramine: Follow-UP and Kinetic Model Selection

Hany A. Elazab
The British University in Egypt, hany.elazab@bue.edu.eg

Military Technical College
Kobry Elkobbah, Cairo,
Egypt.

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CONVERSION OF HEXAMINE DINITRATE INTO DINITRO PENTAMETHYLENE TETRAMINE: FOLLOW-UP AND KINETIC MODEL SELECTION

M. M. Seleet *, S. A. Hassanein* and H. A. El-Azab*

ABSTRACT

Synthesis of cyclotetramethylene tetranitramine through the action of nitrating mixture formed of ammonium nitrate and fuming nitric acid on hexamine in presence of acetic acid, acetic anhydride and p-formaldehyde has been proven. The pathway is relatively long and hexamine dinitrate and dinitro pentamethylene tetramine (DPT) are two of the main intermediate compounds. The former was prepared, purified, and then characterized. Conversion of this compound into the latter has been followed up experimentally. Different kinetic models have been tested.

KEY WORDS

Energetic materials, DPT, Hexamine dinitrate, and Conversion kinetics.

* Egyptian Armed Force.

1. INTRODUCTION

Design of future weapons systems requires the use of energetic material formulations having enhanced performance (energy output) and reduced vulnerability during manufacturing, handling, storage and transportation [1]. Energetic materials are substances or mixtures that react chemically to release energy required for their intended application [2,3].

Synthesis of cyclotetramethylene tetranitramine through the action of nitrating mixture formed of ammonium nitrate and fuming nitric acid on hexamine in presence of acetic acid, acetic anhydride and p-formaldehyde has been proven. The pathway is relatively long and hexamine dinitrate and dinitro pentamethylene tetramine (DPT) are two of the main intermediate compounds [4,5]. The conversion of hexamine dinitrate to DPT was studied from the point of view of kinetics. In this paper, it is intended to study the effect of time and temperature on the conversion rate of hexamine dinitrate to DPT. The application of ordinary kinetic models is also discussed.

2. EXPERIMENTAL WORK

The preparation setup consisted of a flat-bottom 0.5L flask equipped with a mechanical stirrer, three dropping funnels, and a thermometer. Filtration of the prepared samples was done using Buchner funnel - pump system.

2.1 Preparation of hexamine dinitrate

Hexamethylene dinitrate ("hexamine" dinitrate) is an important intermediate in the pathway of preparation of DPT (Dinitro–Pentamethylene-Tetramine). Its preparation involved the addition of a solution of hexamine (10g, 0.07mol) in distilled water (17.5ml, 0.972mol) drop by drop to nitric acid 70% (specific gravity =1.4, 11.75ml, 0.261mol). The reaction temperature was fixed at 15°C; and the rate of hexamine solution addition 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 at 40 °C [6].

2.2 Preparation of DPT from hexamine dinitrate

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

2.3 Follow up the conversion of Hexamine dinitrate into DPT

Preliminary experiments were conducted to investigate the kinetics of conversion 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. Preparations took place according to the procedure stated before. Reaction temperature was varied from 15 to 65°C, reaction time from 0 to 10 hrs. The obtained results were sufficiently accurate and reproducible; hence, a systematic work has been planned for deeply explaining the effects of the mentioned factors. 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 [7, 8]. Lower and higher temperatures have been also investigated during execution of the mentioned reactions.

3. RESULTS

3.1 Yield of prepared compounds

3.1.1 Yield of the hexamine dinitrate

Starting by 10g of hexamine, about 17g of dry hexamine dinitrate was obtained. The average yield was therefore about 89% .The yield; according to the published data is about 95 % [9]. Solubility of small fraction of the product in the spent acid may be the main cause of the recorded disagreement.

3.1.2 Yield of the DPT

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 [6]. Once more the yield was about 65%.

3.2 Results of HPLC analysis

Figure (1) is one of the results obtained by HPLC analysis at varying temperatures (15 °C - 65 °C). 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 $C_{A.}$ and C_A are the initial and final concentrations of hexamine dinitrate respectively. The obtained data and calculated results of HPLC analysis at 45 °C are summarized in table (1). Similar results were obtained at other temperatures.

3.3 Kinetic analysis

3.3.1 Determination of reaction order using homogeneous reaction model

As a first approximation, the reaction may be treated as a homogeneous one. From the concentration results, namely ln ($CA_{.}$ /C_A) and (1/C_A), the rate constant was calculated for first and second order kinetic models respectively as shown in figure (2). The obtained values of rate constant at different temperatures 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.

3.3.2 Calculation of activation energy

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 (3) and (4).

The values of (E/R) are 10470 K and 11573 K and accordingly the activation energy is 87.047 kj/mole and 96.218 kj/mole for the first and second order kinetic models successively.

4. CONCLUSION

Yield of the DPT prepared was about 65%, while that of the hexamine dinitrate prepared was about 89%. Analysis of the prepared samples using an efficient HPLC was a very reliable procedure. The concentrations found at 45°C were not fitting tightly to the ordinary second order kinetic model. Decomposition of hexamine dinitrate became more and more 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 authers [6, 10]. The activation energy applicability of the first order model which gave higher correlation coefficient when compared with the second order one may be opposed by the system heterogeneity.

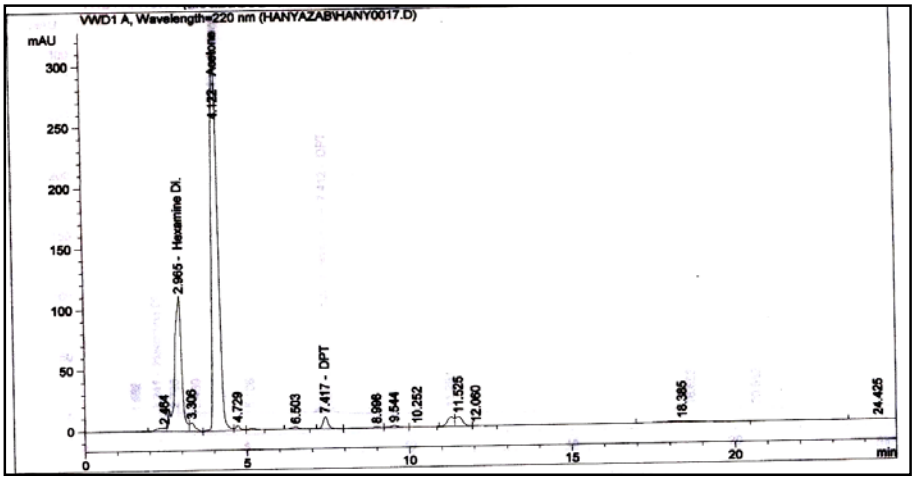

Fig (1) The HPLC chromatogram for the prepared DPT after 15 minutes, at 45°C.

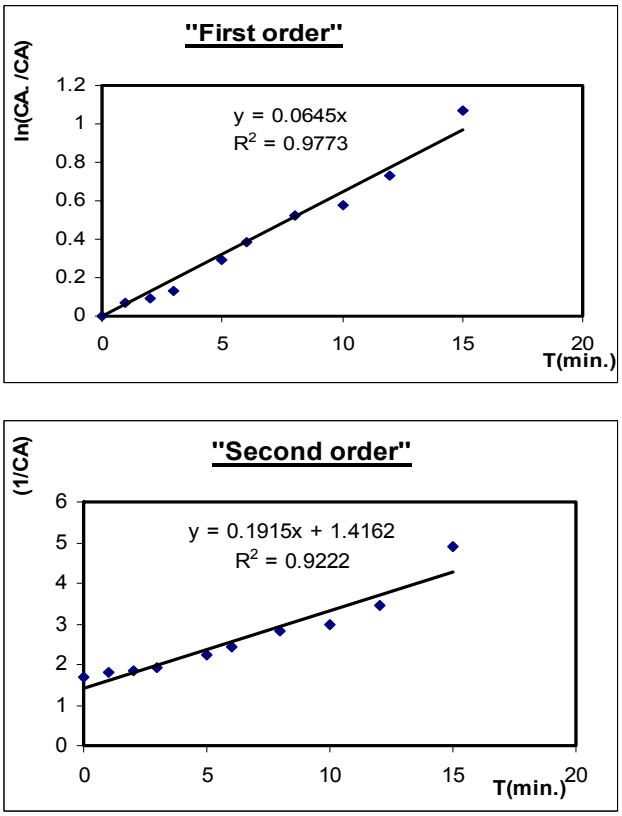

Fig. (2) Representation of the hexamine dinitrate concentration – time data at 45 °C, according to first and second order kinetic models.

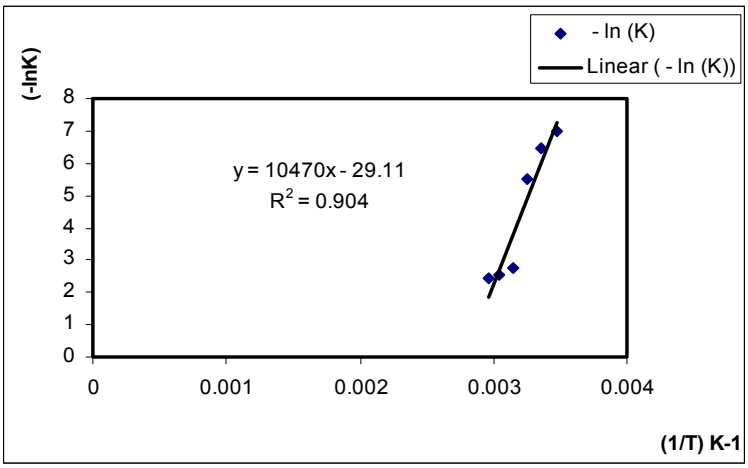

Fig. (3) Activation energy for the conversion of hexamine dinitrate into DPT according to the first order model.

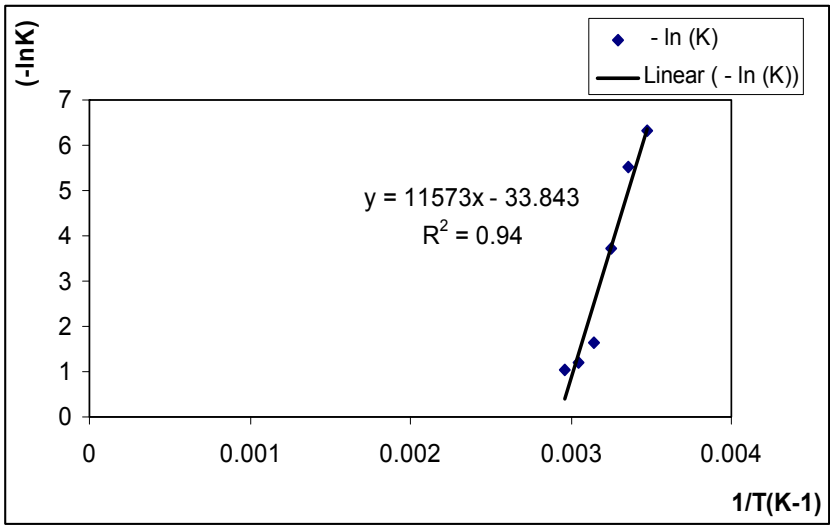

Fig. (4) Activation energy for the conversion of hexamine dinitrate into DPT according to the second order model.

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)	0.59819	0.560087	0.546479	0.52448	0.44564	0.408342	0.353211	0.335965	0.288968	0.20477
DPT (mg / ml)	0	0.0254	0.0378	0.05912	0.125	0.149486	0.19645	0.205188	0.252665	0.3215
ln (C_A/C_A)	0	0.06581	0.090414	0.1315	0.29439	0.381805	0.52684	0.5769	0.72759	1.072

$1/C_A$	1.6717	1.7854	1.82989	1.90665	2.2439	2.44892	2.83116	2.9765	3.46059	4.88352

Table (2) Determined values of reaction rate constant of hexamine dinitrate conversion into DPT at different temperatures for the first and second order kinetic model.

Temperature	**Rate Constant(k)**		**Correlation Factor(R^2)**	
(°C)	1-st order(s^{-1})	2-nd order ($L.mol^{-1}.sec.^{-1}$)	1-st order	2-nd order
15	0.0009	0.0018	0.9956	0.9883
25	0.0016	0.004	0.995	0.9858
35	0.0041	0.0247	0.9908	0.9098
45	0.0645	0.1915	0.9773	0.9222
55	0.0805	0.2985	0.9386	0.8412
65	0.0887	0.347	0.9658	0.8731

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