

3,7-Dinitro-1,3,5,7-Tetraazabicyclo[3,3,1]Nonane (DPT): An Important Intermediate in the Synthesis Route of one of the Most Powerful Energetic Materials (RDX/HMX)

Hany A. Elazab, M. M. Seleet, Said M. A. Hassanein, M. A. Radwan, M. A. Sadek

Abstract: Synthesis of Cyclotetramethylene Tetramine 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. Herein, we report the Preparation of Dinitro Pentamethylene Tetramine (DPT) from Hexamine Dinitrate - as an alternative synthetic route - which is an important intermediate appears through preparation of DPT from Hexamine directly. DPT was prepared at different temperatures. The variation of some factors like: temperature and time has been investigated. The obtained results were reliable and consistent with the literature. The conversion of Hexamine Dinitrate to HMX as another synthetic route was not fully 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. This scientific approach is considered as a bridge through which we aim to initiate a complete kinetic study of an important intermediate in the synthesis route of one of the most powerful energetic materials.

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

I. INTRODUCTION

Energetic materials such as explosives, propellants and pyrotechnics are widely used for both civilian and military applications. Design of future defense systems requires the use of energetic material formulations having enhanced performance (energy output) and reduced vulnerability during manufacturing, handling, storage and transportation. Several important design considerations for such formulations include improved mechanical properties, extended service life and reduced environmental impact in manufacture, use and disposal [1]. Energetic materials are

substances or mixtures that react chemically to release energy required for their intended application.

Bachmann and Sheehan [2] developed a method of preparing DPT. This method involved nitrolysis of hexamine with ammonium nitrate – nitric acid solution and acetic anhydride. The steps of the formation of DPT can be presented according to scheme (1):-[3,4,5]

Hexamine + Acetic acid + Acetic anhydride $44 \pm 1^\circ \text{C}$

Reaction mixture

+ (Ammonium nitrate / Nitric acid) 15 minutes at end of 1st addition

DPT + Spent nitrolyzing medium

Scheme (1) Steps of DPT formation.

Hexamine Dinitrate is an important raw material in production of DPT, hexogen (RDX) and HMX as a source of the methylene base and the simultaneously bound “anhydrous” nitric acid in an advantageous crystalline and relatively stable form[6].

HMX is considered as a powerful military explosive, but it has a limited use due to its high cost. Reported manufacturing processes for HMX involves the nitration of hexamine. It is well known that HMX can be prepared from DPT, which has been identified as a key intermediate in the formation of HMX from the nitration of hexamine, which is also known as the modified Bachmann process as previously mentioned.

Direct nitrolysis of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1] nonane (DPT) is a feasible way to synthesize HMX, and it has multiple practical applications. A new nitrolysis process involving the use of an $\text{N}_2\text{O}_5\text{-HNO}_3$ system catalyzed by acidic ionic liquids (AILs) was developed [7].

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].

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II. EXPERIMENTAL WORK

2.1. Raw Materials and Instrumental Analysis

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. 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. To handle these kinds of energetic materials, best safety practices (leather gloves, face shield) are strongly recommended. An "IA - 9100 series" Digital melting point apparatus was used to measure the melting point of both the standard and the prepared samples. For each substance, three consecutive trials were performed and the average value of the melting point (m.p.) was calculated.

Carbon, Hydrogen and Nitrogen were determined using a Perkin-Elmer 2400, CHN Elemental Analyzer equipped with AD-4 auto balance. A deflagration test apparatus of Chilworth Technology Company was used to determine the ignition temperature of the prepared samples as a characteristic property indicating the sensitivity to heat.

A Shimadzu 8100 series FTIR spectrophotometer has been used to obtain the FTIR spectrum for the prepared samples.

A Shimadzu UV-vis. spectrometer double beam, UV-1700, has been used to run spectroscopic analysis of the prepared Hexamine Dinitrate, DPT, and HMX by measuring its wave length at maximum absorption. The selected operating conditions were: Wavelength range: from 600 to 190 nm, Scan speed: medium, Sampling interval: 1 nm, and Measuring mode: absorbance.

High Performance Liquid Chromatography (HPLC) can also be employed not only for separation 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 used in this experimental work was Agilent 1100 series HPLC instrument.

The sensitivity to impact was determined by applying standard method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion (h 50%) of the sample. The friction sensitivity of the samples was determined until there was no explosion/ignition in five consecutive test samples at that assigned weight. The results obtained for impact and friction sensitivity tests were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively. Chemicals used in this work were chosen carefully to achieve the required specifications and requirements for the previously planned experimental work, as described in Table 1.

Table (1) Specifications of materials used during the experimental work

Name	Formula	Source	Molar mass (g/mol)	ρ(g/ml)	m.p. (°C)
Hexamine (> 99%)	(CH ₂) ₆ N ₄	Reizt die Augen, Germany	140.19	1.33 (g/cm ³)	At 260 decompose

Glacial acetic acid (99.9%)	CH ₃ CO OH	Tedia Company Inc, USA	60	1.049	15-16
Ammonium nitrate (97%)	NH ₄ NO ₃	VED, LaBorHE MIE APOIDA,	80.04	1.73 (g/cm ³)	decomposition starts above 170
P-formaldehyde (90%)	HO(CH ₂ O) _n H	Win lab, U.K	30.03	0.815 (g/cm ³)	--
Fuming nitric acid (99%)	HNO ₃	AZC, Egypt	63	1.5	--
Nitric acid (70%)	HNO ₃	AZC, Egypt	63	1.4	--
Acetic anhydride (99.6%)	(CH ₃ CO) ₂ O	Tedia Company Inc, USA	102	1.082	-74.13
RDX	(CH ₂ N) ₃ NO ₂ ₃ C ₃ H ₆ O ₆ N ₆	AZC, Egypt	222.13	1.767	α (203.5) β(204.1) γ (206-207) β 247, α 257
HMX	(CH ₂ N) ₄ NO ₂ ₄ C ₄ H ₈ O ₈ N ₈	AZC, Egypt	296.17	1.89	γ 280, δ 281.5 generally, >240

2.2. Synthesis of Hexamine Dinitrate from Hexamine

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.

2.3. Synthesis 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.

2.4. Following up the Conversion and the Yield of Hexamine Dinitrate into DPT



2.4.1. Variation of Temperature and Time

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).

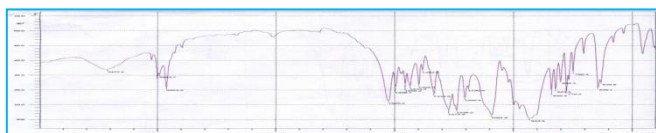
2.4.2. High Performance Liquid Chromatography as a Monitoring Technique

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. FTIR Analysis



The prepared DPT showed IR absorptions at 3031, 2974, 2937 and 2880 cm⁻¹ assignable to asymmetric and symmetric vibrations of methylene groups of DPT. The IR frequencies (Fig. 5) at 1602 and 1524 cm⁻¹ corresponds to asymmetric stretching vibrations of nitro group and symmetric stretching vibrations observed in 1289 cm⁻¹.

Generally, vibrations of organic molecules can be divided into two types; vibrations associated with the molecule as a whole and vibrations associated with the present functional groups. Employing one of the modern FTIR spectrometer, the obtained IR spectrum is usually ranged from 4000 cm⁻¹ to 250cm⁻¹. The vibrations characterizing the molecule as a

whole usually give rise to absorption bands below 1300 cm⁻¹. These bands are useful for identification of the unknown molecules by comparing their spectrum to that of authentic known standard molecules. This region is often called the "fingerprint region".

The vibrations associated with the functional groups give usually absorption bands above 1500 cm⁻¹. These bands are useful in qualitative analysis of the unknown organic matter. Two characteristic intense bands are always associated with the NO₂ group. These bands can be attributed to the symmetric (ν_s) and asymmetric (ν_{as}) vibrations of the mentioned group. For the prepared HMX and DPT, the IR absorption bands found using the 8100 series FTIR spectrophotometer are presented in Table (1).

Table (1) IR absorption bands for prepared DPT and HMX.

The stretching vibrations of the (N-NO ₂) bond in Nitramines (cm ⁻¹)	The CH stretching mode (cm ⁻¹)		The Intense NO ₂ stretching bands (cm ⁻¹)		Compound
	ν _s	ν _{as}	Band at	Band at	
Prepared DPT	ν _s	1334.6	2923.9	1272.9	1525.6
	ν _{as}	1525.6			
Prepared HMX	ν _s	1390.6	3072.4	1271,1315	1535,1572
	ν _{as}	1571.9			

The experimentally determined sensitivity test results of DPT indicated its impact insensitive [*h*_{50%} explosion, 45 cm] and friction insensitive [up to load of >37 kg]. These results suggest the overall low vulnerability to mechanical stimuli compared to that of other nitramines energetic materials such as RDX and HMX (friction insensitive up to 15 and 18 kg, respectively). Therefore, appropriate strict safety measures must be applied during DPT usage in the synthesis of the powerful energetic materials such as RDX and HMX.

3.2. UV – Vis. Analysis

In the ultraviolet region, the electronic transitions occurring and also on the effect of the atomic environment on these transitions. The obtained absorbance regions and also the values of the maximum absorbance wave length are given in Table (2).

Table (2) UV Absorbance regions and maximum absorbance for the prepared compounds

No.	Compounds	Maximum absorbance "λ _{max} " (nm) in methanol	Maximum absorbance "λ _{max} " (nm) in ethanol	Absorbance region (nm) (from literature)
1	Prepared Hexamine dinitrate	222	204	200 to 240 [16]
2	Prepared DPT	248	203	200 to 250[16]
3	Prepared HMX	233	222	200 to 270[16]

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Since λ_{max} of Hexamine dinitrate is very close to that of the DPT when ethanol is employed as a solvent, λ_{max} of HMX is also very close to that of RDX. From these results, it is clear that identification of the prepared compounds via their UV spectra is somewhat difficult.

3.3. Organic Element Microanalysis

Table (3) Elemental analysis of the prepared compounds.

Compound		C (%)	H (%)	N (%)
Hexamine dinitrate	Pure	27.06	5.26	31.57
	Prepared	26.91	5.29	31.745
DPT	Pure	27.52	4.58	38.53
	Prepared	27.21	4.536	38.094
HMX	Pure	16.21	2.70	37.84
	Prepared	16.84	2.8	39.29

Referring to characteristics of the pure compounds, it is clear that the prepared compounds are of good quality. The yield is also acceptable.

3.4. Ignition Temperature Values

Table (4) ignition temperature results on HMX

Compound	Ignition temperature " $T_{ignition}$ " °C
Standard RDX	≈ 220 °C (215 – 230 °C)
Standard HMX	≈ 287 °C (280 – 300 °C)
HMX prepared	265°C

3.5. Melting Point Values

Table (5) Melting points of the prepared compounds.

III. COMPOUND	Measured m.p. (°C)	m.p. (from literature) (°C)	Remarks
DPT	prepared 213	--	Nearly pure
	pure --	213 [7], [11]	DPT crystals
Hexamine dinitrate	prepared 160	--	Nearly pure
	pure --	160 [11]	Hexamine dinitrate crystals
HMX	prepared 260 - 265	--	RDX is the
	pure --	276-285 [3],[7],[9]	probable side product

3.6. HPLC Analysis as a tool in calculating the yield of prepared compounds

The following figures (1-5) are representing some selected results obtained by HPLC analysis for standard and prepared compounds. There is some more figures show the chromatograms obtained at the end of the investigated reaction time. By examining the obtained chromatograms, the prepared compounds were identified qualitatively and quantitatively to calculate the conversion and yield percentage as in tables (2-11).

3.6.1. Yield of the Hexamine Dinitrate

Characteristics of the obtained Hexamine Dinitrate were found and given in Tables shown below. 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.

3.6.2. Yield of the DPT

Characteristics of the prepared DPT were found and presented in Tables shown below. 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 °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 °C by adding a suitable quantity of ice. The product was then filtered and dried under vacuum. Once more the yield was about 65%.

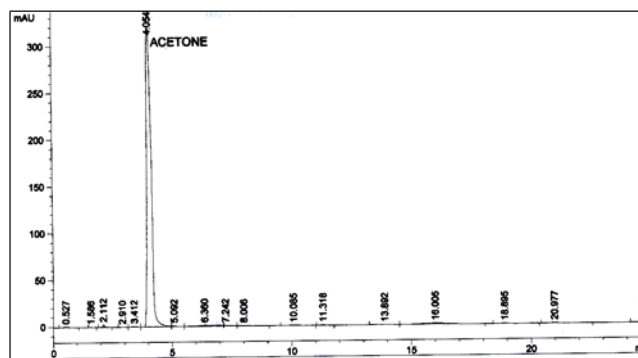


Fig. (1) HPLC Chromatogram of standard Acetone

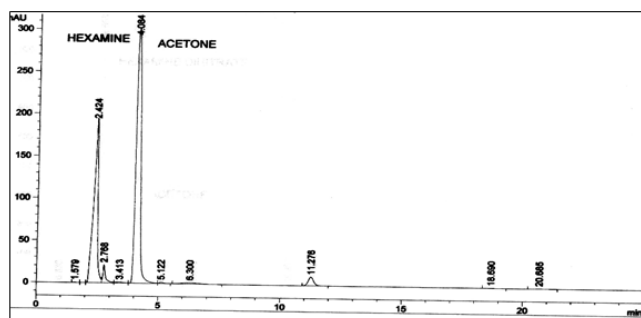


Fig. (2) HPLC Chromatogram of standard Hexamine

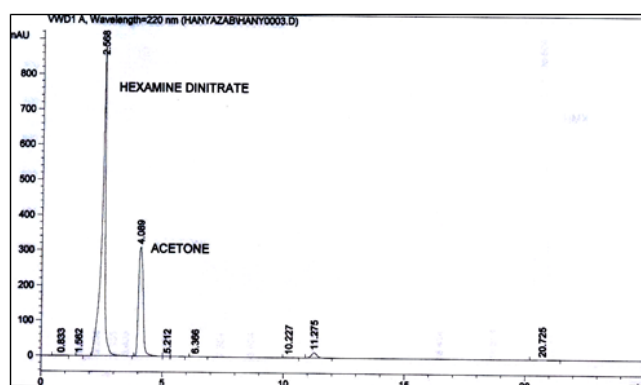


Fig. (3) HPLC Chromatogram of prepared hexamine dinitrate

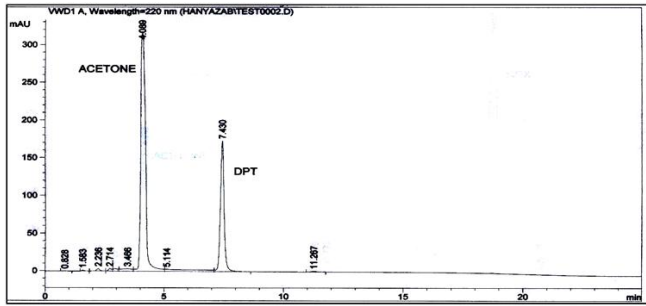


Fig. (4) HPLC Chromatogram of prepared DPT

3.7. HPLC Analysis for calculating conversion and yield at different temperatures

3.7.1. Interpretation of the results obtained at 15 oC

The reaction is generally very slow. 600 minutes were sufficient to convert about 40% only from hexamine dinitrate into DPT.

Table (6) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 15 °C.

Time (min.)	0	5	10	15	120	240	360	480	600
Hexamine dinitrate (mg / ml)	0.592695	0.58921	0.58701	0.58359	0.54164	0.48039	0.44791	0.38552	0.35588
DPT (mg / ml)	0	0.00152	0.00280	0.00509	0.03200	0.07230	0.10200	0.12600	0.13500

Table (7) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 25 °C.

Time (min.)	0	5	10	15	120	240	360	480	600
Hexamine dinitrate (mg / ml)	0.59780	0.58660	0.58502	0.58129	0.48863	0.40006	0.32762	0.29629	0.23547
DPT (mg / ml)	0	0.00593	0.00749	0.00985	0.08700	0.16200	0.21500	0.23100	0.23500

Table (8) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 35 °C.

Time (min.)	0	5	10	15	120	240	360	480	600
Hexamine dinitrate (mg / ml)	0.58809	0.53282	0.52159	0.45800	0.3694	0.20273	0.1340	0.08620	0.05255
DPT (mg / ml)	0	0.03425	0.05046	0.10219	0.1785	0.31534	0.3684	0.40172	0.43891

Table (9) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 45 °C.

Time (min.)	0	1	2	3	5	6	8	10	12	15
Hexamine dinitrate (mg / ml)	0.5982	0.56009	0.54648	0.5245	0.4456	0.40834	0.35321	0.33597	0.28897	0.2048
DPT (mg / ml)	0	0.02540	0.03780	0.0591	0.1250	0.14949	0.19645	0.20519	0.25267	0.3215

3.7.5. Interpretation of the results obtained at 55 °C

The concentrations and concentration terms found at 55 °C were neither fitting tightly to the first order nor to the second order ordinary kinetic models. The reaction at this temperature was faster. About 74% of the hexamine dinitrate were depleted during the first fifteen minutes. The formed DPT was somewhat less than the theoretical. This may be attributed to some sort of the side reactions. This may also explain the recommendation given by many authors which limit the reaction temperature to 45 °C.

Table (10) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 55 °C.

Time (min.)	0	5	10	15
Hexamine dinitrate (mg / ml)	0.59698	0.40825	0.32540	0.15522
DPT (mg / ml)	0	0.13400	0.18750	0.27640

3.7.2/ Interpretation of the results obtained at 25 oC

The rate of conversion of hexamine dinitrate into DPT at 25 °C was found relatively higher than that at 15 °C. Depletion of about 60% of hexamine dinitrate was achieved after 600 minutes.

3.7.3. Interpretation of the results obtained at 35 oC

The reaction rate was appreciably higher than that found below this temperature. About 90% conversion was recorded after 600 minutes.

3.7.4. Interpretation of the results obtained at 45 oC

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 [15, 16].

3.7.6. Interpretation of the results obtained at 65 oC

The concentrations and concentration terms found at 65 °C were neither fitting tightly to the first order nor to the second order ordinary kinetic models. The reaction was as usual faster. About 77% of the hexamine dinitrate were depleted in the first fifteen minutes. The DPT yield was less than that found in the literature.

Table (11) DPT and hexamine dinitrate concentrations and concentration terms at different reaction times at 65 °C.

Time (min.)	0	5	10	15
Hexamine dinitrate (mg / ml)	0.59780	0.39850	0.28370	0.14048
DPT (mg / ml)	0	0.14200	0.19230	0.26235



The fractional conversion "X_A" of hexamine dinitrate and the yield "Y" of DPT were calculated at each investigated reaction time. For easy comparison, the results of conversion and yield at different reaction times for all temperatures were collected in tables (12 - 15); and figures (5 - 8).

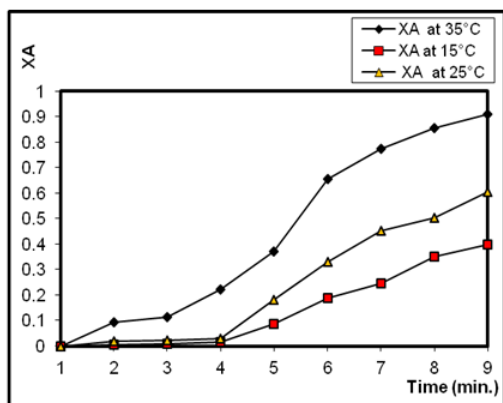


Fig. (5) Conversion of hexamine dinitrate versus time between 15 and 35 °C.

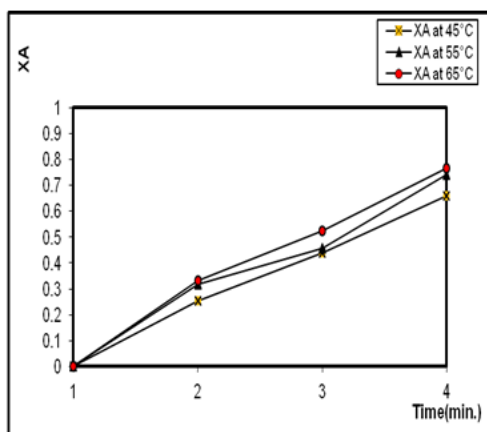


Fig. (6) Conversion of hexamine dinitrate versus time between 45 and 65 °C.

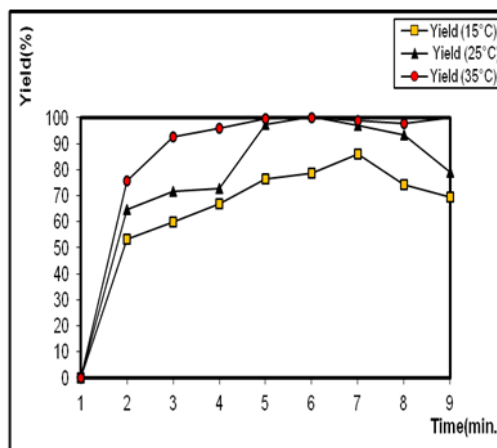


Fig. (7) Yield of DPT versus time between 15 and 35 °C.

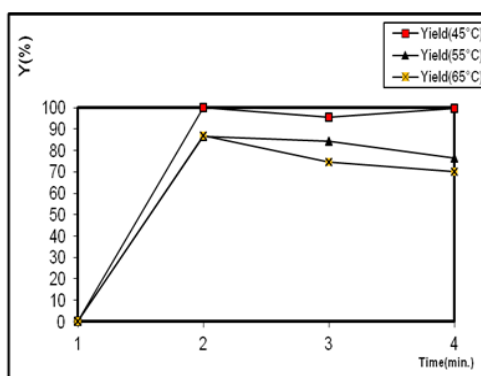


Fig. (8) Yield of DPT versus time between 45 and 65 °C.

Table (12) Calculated results of hexamine dinitrate conversion at different reaction times and at tested temperatures.

Point number	1	2	3	4	5	6	7	8	9
Time (min.)	0	5	10	15	120	240	360	480	600
XA (%) at 15°C	0	0.005879	0.00959	0.01536	0.08614	0.18948	0.24428	0.34954	0.39955
XA (%) at 25°C	0	0.0187	0.02137	0.02761	0.1826	0.33078	0.451957	0.50436	0.6061
XA (%) at 35°C	0	0.09399	0.11308	0.2212	0.37187	0.65527	0.7721	0.853425	0.910633

Table (13) Calculated results of hexamine dinitrate conversion at different reaction times and at tested temperatures.

Point number	1	2	3	4
Time (min.)	0	5	10	15
XA (%) at 45°C	0	0.25502	0.43836	0.6576
XA (%) at 55°C	0	0.31614	0.45492	0.74
XA (%) at 65°C	0	0.33338	0.5254	0.765

Table (14) Calculated results of DPT yield at different reaction times and at tested temperatures.

Point number	1	2	3	4	5	6	7	8	9
Time (min.)	0	5	10	15	120	240	360	480	600
Yield(15°C)	0	53.2	59.987	66.97	76.47	78.55	85.96	74.209	69.557
Yield(25°C)	0	64.582	71.56	72.81	97.239	100.2713	97.098	93.48	79.1386
Yield(35°C)	0	75.6	92.58	95.846	99.591	99.846	98.996	97.66	100.0039

Table (15) Calculated results of DPT yield at different reaction times and at tested temperatures.

Point number	1	2	3	4
Time (min.)	0	5	10	15
Yield(45°C)	0	99.98	95.477	99.71
Yield(55°C)	0	86.634	84.241	76.34
Yield(65°C)	0	86.93	74.7	70

IV. CONCLUSION

The work reports the synthesis, characterization, mechanism, effect of temperature and time variation, and some selected safety performance evaluation of one of the most important key precursor (DPT) in the field of high energetic materials synthesis. The DPT is an important and key intermediate for the synthesis of two most widely used benchmark military explosives namely RDX and HMX. The data shed light on DPT from the point of safety during its use as an intermediate for the synthesis of RDX and HMX. Recently, research efforts are devoted to enhance the performance of energetic materials using nanocomposites and nanoparticles due to its unique effect not only in the energetic materials field but also in medical, environmental, and industrial applications.[17-41]

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 obtained results were reliable and consistent with the literature. The conversion of Hexamine Dinitrate to HMX as another synthetic route was not fully studied from the point of view of kinetics. This scientific approach is considered as a bridge through which we aim to initiate a complete kinetic study of an important intermediate in the synthesis route of one of the most powerful energetic materials.

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