

Decomposition of multi-peroxidic compounds Part II. Hexamethylene triperoxide diamine (HMTD)

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Abstract

The thermal decomposition of neat hexamethylene triperoxide diamine (HMTD) was examined over the temperature range 100 and 180 °C. It was found to be first-order up to 150 °C and produce ~2 mole of gas/mole HMTD; primarily CO₂ but also trimethylamine and ammonia. Above 150 °C, the decomposition became nearly instantaneous and gas production more than doubled. Instead of carbon dioxide, CO was the main product (about 3 mole/mole HMTD) and under air no trimethylamine was observed from the thermolysis. The observed changes in products may indicate a change in mechanism, but they can also be explained by a secondary reaction, the oxidation of trimethylamine to HCN and methanol. The latter interpretation is based on the fact that when available oxygen was limited, i.e. when the decomposition was performed under vacuum, some trimethylamine was observed in the high temperature thermolysis. Two possible mechanisms are suggested, one free radical and the other ionic. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hexamethylene triperoxide diamine; DSC

1. Introduction

Hexamethylene triperoxide diamine (HMTD) was first synthesized around 1900 and initial studies focused on its synthesis and on determining its structure [1]. As late as 1967 Urbanski proposed two possible structures for HMTD, but by 1984 NMR showed the structure to be that first proposed in 1900 (Fig. 1) [2]. This was confirmed a year later by X-ray crystallography and more recently by density functional theory calculations [3,4]. The structure of HMTD is unusual because the N(CH₂)₃ group is exactly planar and symmetrical about the bridgehead nitrogens, the extreme sensitivity of HMTD may be

related to this feature. In the 1940s and into the 1960s the military examined HMTD for possible applications; [2,5] however, its extreme sensitivity made commercial or military applications unsafe. Recently, it has found use by terrorists because of ease of synthesis and availability of starting materials [6]. The present study is part of a series examining the stability of multi-peroxidic compounds under the influence of electron impact or thermal decomposition [7,8].

2. Experimental section

Synthesis of HMTD, both labeled [¹⁵N(¹³CH₂O–O¹³CH₂)₃¹⁵N] and unlabeled, has been previously reported [7]. The basic synthetic procedure used hexamethylene tetramine and hydrogen peroxide with

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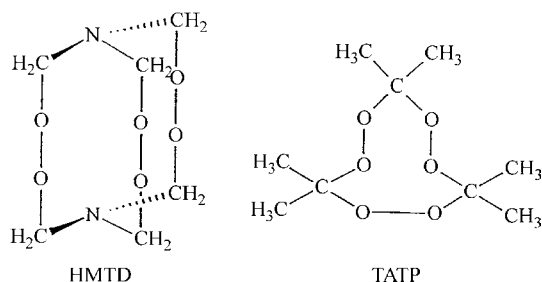


Fig. 1. Structure of HMTD and TATP.

citric acid catalyst [4]. As prepared, HMTD is a white crystalline solid, insoluble in water and common organic solvents such as methanol, acetonitrile and acetone. Although, HMTD has slight solubility in chloroform (0.64 g/100 g), [1] its solubility was too low to use conventional liquid chromatography and it was too labile to permit use of gas chromatography to determine kinetics. Complete decomposition of HMTD at low temperatures, such as in the isothermal studies described below, left a small amount of colorless liquid (which is probably trimethylamine). However, in differential scanning calorimetry (DSC) studies, which took HMTD to very high temperatures, only a very small amount of black or brown residue remained.

The thermal stability of HMTD was evaluated using DSC. Samples (0.1–0.4 mg) were sealed in capillary tubes (1.5 mm o.d. \times 10 mm) which were held in an aluminum cradle [9] under nitrogen flow inside the head of a TA Instruments 2910 DSC, which was calibrated against indium. The thermograms of HMTD were obtained over the temperature range 40–500 °C. The American Society for Testing and Materials (ASTM) differential heating rate method was used to calculate Arrhenius parameters [10]. A plot of $\log_{10} \beta$ (β is heating rate in °C min⁻¹) versus $1/T$ (T is the exothermic peak temperature in kelvin) was made. An approximation of the activation energy (E_a) could be calculated from the slope, $-2.19R[d(\log_{10} \beta)/d(1/T)]$ (where R is the gas constant). A refinement of the activation energy and an estimation of the Arrhenius pre-exponential factor (A) were calculated according to the ASTM protocol [10].

Isothermal thermolyses were performed in an oven on samples (0.1–0.6 mg) in tubes 4 mm o.d. \times 50 mm to measure kinetics or in narrower tubes (1.2–1.5 mm

o.d. \times 50 mm) to determine decomposition gases. Total decomposition was estimated by heating HMTD until no further gas formed. This was used to determine the fraction reacted for calculation of kinetics. After the sample was heated for a specified time interval, the tube was broken into a gas manometer (to assess amount of gas produced) or into a GC (to assess gas composition). The decomposition gases were identified by gas chromatography/mass spectrometry (GC/MS) [11]. A HP Model 5890 Series II GC, equipped with model 5971 electron impact mass selective detector, helium carrier gas and PorapLOT Q (0.25 mm \times 25 mm) column from Chrompack was used [11]. Decomposition gases were identified by comparing their GC retention times and mass spectra to authentic samples. When authentic samples were not available, sample spectra were compared with the NIST MS library for tentative assignment. To quantify the permanent gases, a HP 5890 series II GC with a thermal conductivity detector (GC/TCD) and Hayesep DB 100/120 (30 in. \times 1/8 in.) column (Alltech) was used.

3. Results

A typical DSC scan of HMTD, shown in Fig. 2, consisted of a single sharp exotherm at about 165 °C ($\theta = 20$ °C min⁻¹). Arrhenius parameters were calculated from the DSC data using the ASTM method. At 150 °C and below first-order rate constants were calculated from isothermal heating (Table 1). However, at 160 °C HMTD decomposition went from 90% remaining to 0% remaining in the first 45 s. Arrhenius parameters derived by the DSC variable heating rate method ($E_a = 164.7$ kJ/mol, $A = 1.49 \times 10^{18}$ s⁻¹) and those derived from monitoring evolved gas ($E_a = 107$ kJ/mol, $A = 4.21 \times 10^{10}$ s⁻¹) are given in Table 1. These parameters differ significantly and the isothermal results should be those relied on. However, it is interesting to note the rate constants calculated from these parameters do not differ greatly, an example of the kinetic compensation effect [12].

To analyze for the decomposition products of HMTD, samples were heated in air and in vacuum over the temperature range 100–180 °C. GC/MS was used to identify the products and GC/TCD to quantify them. GC/TCD analysis indicated that the prominent

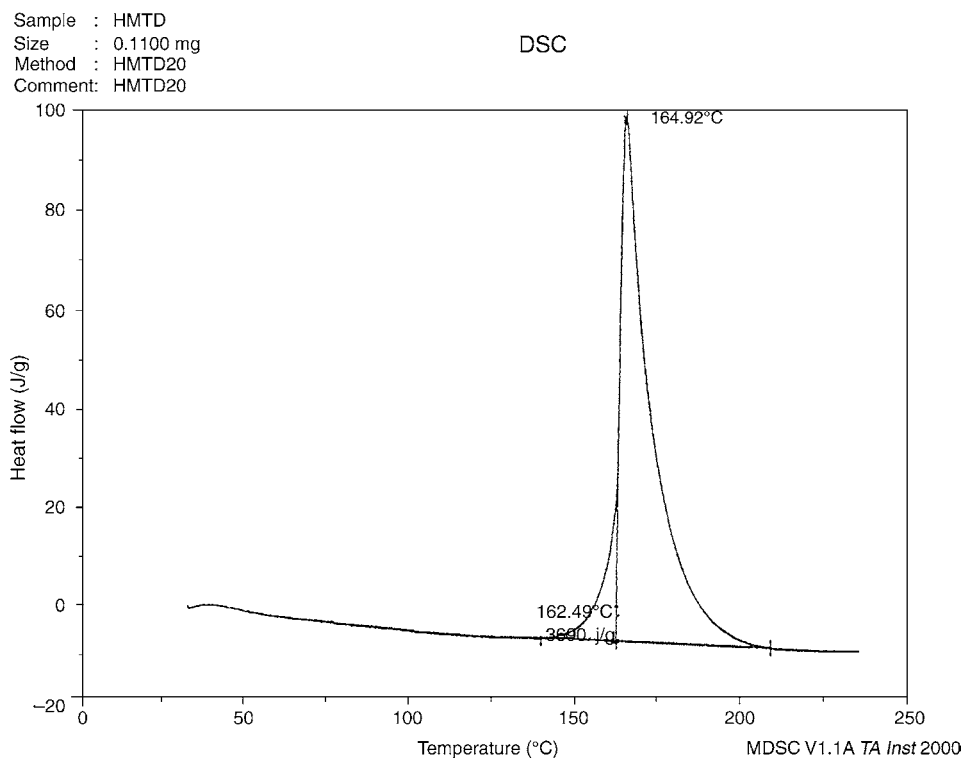
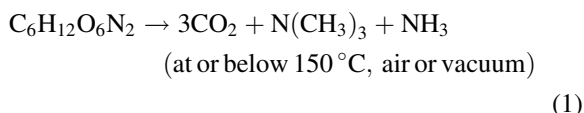


Fig. 2. DSC Thermogram of HMTD ($20\text{ }^{\circ}\text{C min}^{-1}$).

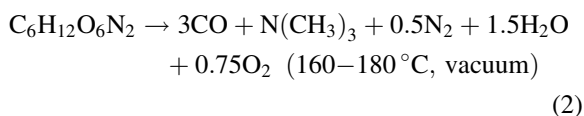
gas at $150\text{ }^{\circ}\text{C}$ and below was CO_2 , at $160\text{ }^{\circ}\text{C}$ and above there was a major change in the decomposition products just as there was in the kinetics. CO_2 became the minor carbonaceous gas and CO , the major one (Table 2). At or below $150\text{ }^{\circ}\text{C}$ the fate of nitrogen was to form trimethylamine and presumably ammonia (Fig. 3, Eq. (1)). Trimethylamine was readily identified by GC/MS but was not quantified. By the GC/MS technique it was difficult to differentiate between ammonia and water. Both had retention times of about 19 min and masses 17 and 18 were both prominent fragments. We believe the peak at 19 min is a mixture of water and ammonia and a water/ammonia mixture produced similar fragmentation patterns.

At 160 and $180\text{ }^{\circ}\text{C}$, trimethylamine was not observed in the thermolyses performed in air; however, it was observed in those performed in vacuum (Figs. 4 and 5). Eq. (2) is meant to convey the basic products from the high-temperature thermolysis of HMTD; however, it should be noted that the formation of molecular oxygen was not observed. Several

oxygenated hydrocarbons were observed instead; oxygen appears in this formula only for the sake of simplicity and stoichiometry.



HMTD



We suspected the reason trimethylamine was not observed in the high temperature thermolysis was due to its reactivity. A literature search revealed that trimethylamine reacts with molecular oxygen at temperatures as low as $165\text{ }^{\circ}\text{C}$, though the reaction does not go to completion [13]. Cullis and Waddington [13] studied the oxidation of trimethylamine and triethylamine and found their oxidations self-inhibiting.

Table 1
DSC and isothermal kinetics

Scan rate, β (°C/min)	Exothermic maximum temperature		Heat released		Number of runs	T (°C)	K	R^2	Fraction remained (%)	Atmosphere	T (°C)	k (ASTM)	k (gas)
	°C	K	J/g	cal/g									
DSC exotherms of HMTD at various scan rates ^a						Isothermal first-order rate constants for neat HMTD ^b				Rate constants calculated from Arrhenius parameters			
20	164	437	3285	793	3	100	4.95E–05	0.96	0.070	Air	100	6.2E–06	3.0E–05
10	157	431	3418	825	3	120	2.96E–04	0.95	0.082	Air	150	3.6E–03	1.8E–03
5	152	426	4255	1027	2	140	1.14E–03	0.95	0.299	Air			
2.5	146	419	4143	1000	3	150	3.26E–03	0.95	0.440	Air			
1	138	411	4207	1016	2	160	Completely gone in less than 45 s			Air			
						160				Vacuum			

^a E_a (kJ/mol) 165 = 39.4 kcal/mol; A (s^{-1}) $1.5E+18$, $R^2 = 0.998$ DSC.

^b Neat 100–150°C, E_a (kJ/mol) 107 = 25.5 kcal/mol, A (s^{-1}) $4.21E+10$, $R^2 = 0.995$ isothermal.

Table 2
HMTD decomposition products under various experimental conditions

	Temperature (°C) atmosphere																												
	180 °C					160 °C				150 °C			140 °C			120 °C				110 °C		100 °C							
	Vacuum ^a	Vacuum	Air ^a	Air	Air	Vacuum	Vacuum	Air	Air	Vacuum	Air	Air	Vacuum	Air	Air	Vacuum	Air	Air	Air	Vacuum	Vacuum	Air	Air	Vacuum	Vacuum	Air	Air	Vacuum	
Hours heated	0.67	0.67	0.67	2.25	0.7	1	1.67	1	0.5	4.25	4.75	3.5	4	9.5	21.33	11.5	17.3	2.75	30	1	1.25	25.25	40.3	1.75					
Fraction decomposed	1	1	1	1	Label	1	1	1	1	1	1	1	1	1	1	1	1	1	0.17		0.05	1	1	Label					
Sample (mg)	0.13	0.12	0.18	0.10	0.14	0.11	0.19	0.42	0.39	0.15	0.13	0.22	0.27	0.29	0.31	0.36	0.30	0.40	0.29	0.75	0.45	0.38	0.50	0.57					
mol gas/mol HMTD																													
N ₂	0		0.2	0.3		0		0.10	0.4	0	0.10	0	0	0	0			0.12	0.04					0.00					
CO ₂	0.2		0.4	0.4		0.3		0.3	0.3	1.4	2.0	2.1	1.9	2.0	1.9			1.9	1.9					1.9					
CO	2.6		3.9	3.8		3.1		3.1	2.9	1.1	0.2	0.1	0.2	0.2	0.1			0.1	0.1					0.1					
Total gas by GC	2.9		4.5	4.5		3.3		3.5	3.3	2.5	2.2	2.2	2.0	2.1	2.0			2.1	2.0					2.0					
Total gas by manometer	3.9		6.1	6.1		2.8		5.1	5.0	1.9	3.1	1.8	2.6		1.6			2.4	2.4					2.3					
GC estimates of relative amounts (%)																													
CO ₂	14	100	80	100	100	74	100	100	100	40	47	33	51	61	59	29.1	61	66	100	100	100	61	58	100					
N(CH ₃) ₃	27	73	–	–	–	100	79	–	–	100	100	100	100	100	100	100	100	100	t	13	18	100	100	35					
CO	4.8	t	s	31	22	36	2.4	7.7	70	55	t	t	t	t	t	t	t	t	–	t	t	–	t	t	0.8				
HCN	21	–	–	12	7	13	–	–	14	s	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NH ₃ /H ₂ O	19	s	s	s	10	s	s	s	10	3.0	s	s	s	s	s	1.9	s	s	2.9	s	s	1.7	3.9	3.2	2.1	3.1			
HCOOCH ₃	24	t	t	t	t	t	2.5	t	8	t	t	s	t	t	t	t	t	t	t	–	t	–	t	t	–				
N ₂	3.5	t	–	11	13	14	–	–	15	11	–	2	1	–	2.3	1.9	t	2.5	2.5	9.4	–	–	–	–	2.2	1.8	–		
O ₂	3.9	t	–	t	–	t	–	–	–	–	–	1.0	0.5	–	0.6	0.4	–	1.1	0.9	–	–	–	–	–	0.7	0.7	–		
CH ₃ OH	22	–	t	t	t	t	t	t	13	9	t	t	t	t	t	t	t	t	t	–	–	–	–	–	t	t	–		
CH ₃ CN	26	–	t	t	t	t	t	6	s	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
(CN) ₂	–	–	–	t	t	t	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CH ₃ COOH	29	–	–	–	–	t	–	–	14	t	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
HCOOH	27	–	–	–	–	t	–	–	t	–	–	–	–	–	–	–	–	–	–	–	t	–	–	–	–	–	–	–	2.4

Below detection limits: (–); RT: retention time (min); t: trace; s: some.

^a Atmospheric conditions.

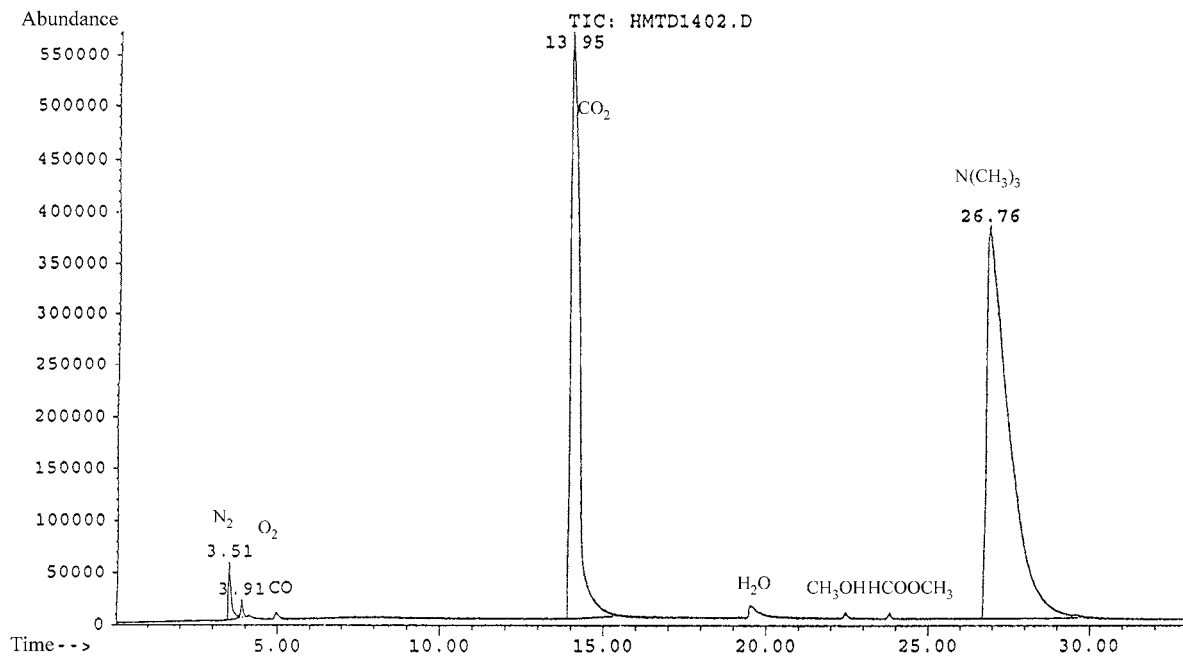


Fig. 3. Chromatogram HMTD heated in air 140 °C.

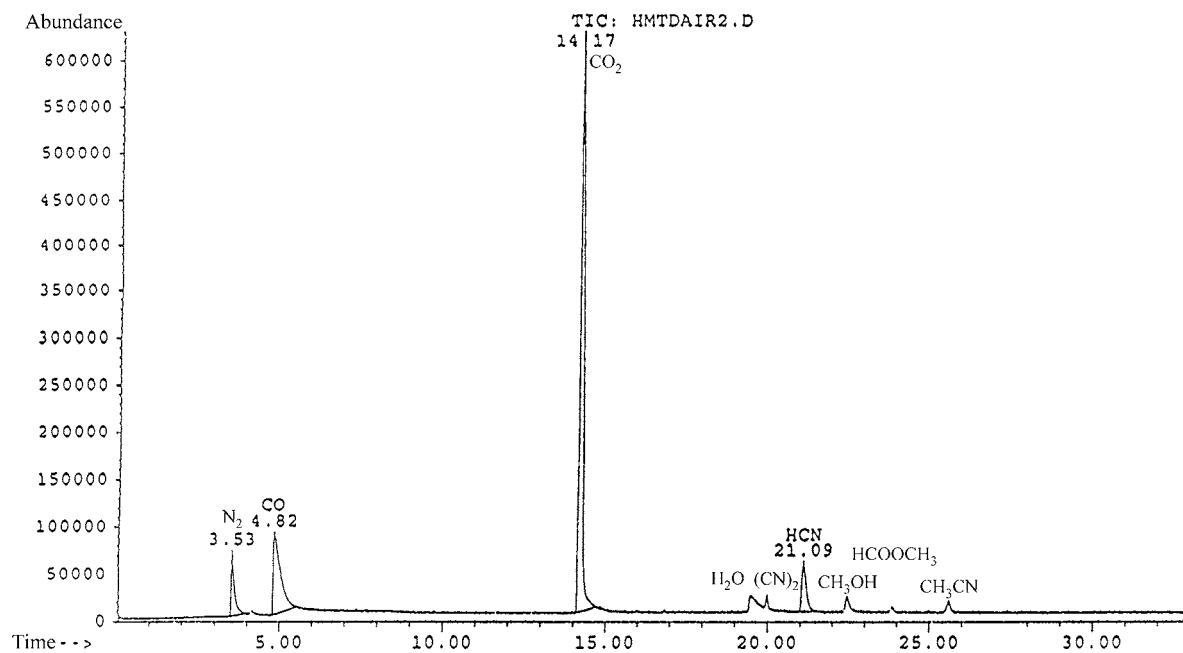


Fig. 4. Chromatogram HMTD heated in air 180 °C.

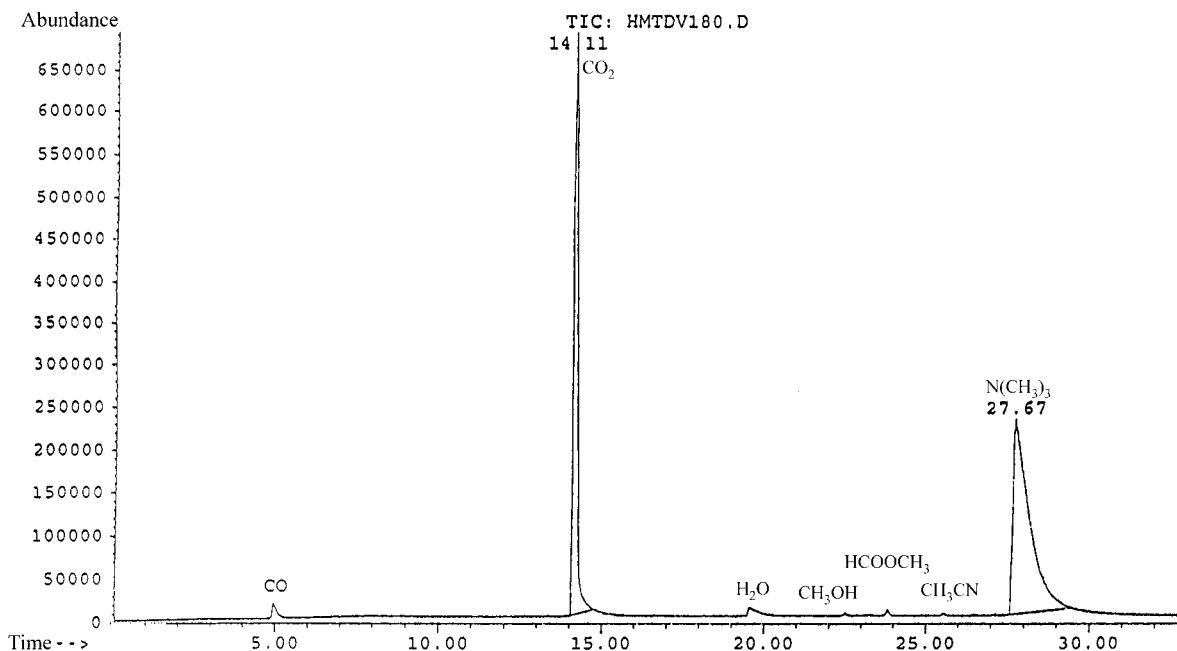
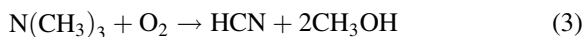


Fig. 5. Chromatogram HMTD heated in vacuum 180 °C.

Triethylamine decomposed by two routes, forming monoethylamine by the unimolecular decomposition of an intermediate peroxy-radical, or producing diethylamine by capping of the peroxy radical to form a hydrogen peroxide which then reacted with a second molecule of triethylamine to form the diamine and acetaldehyde. In contrast, the oxidation of trimethylamine did not produce mono-methylamine, it formed formaldehyde, dimethylamine and nitrogen. The authors speculated that steric hindrance made oxidation of trimethylamine difficult.

In the thermolysis of HMTD we observed neither formaldehyde nor dimethylamine. Our experimental conditions are such that we would not expect to observe formaldehyde, but dimethylamine should be observable if formed. This difference in decomposition products may be due to differences in experimental conditions (although the temperature and reactant concentrations are similar); or perhaps, in the decomposition of HMTD, oxygen is reacting with a trimethylamine precursor. From examination of the decomposition products of HMTD at 160 and 180 °C in vacuum and in air, we surmised that the ultimate fate of trimethylamine or its precursor is to be

converted to hydrogen cyanide and methanol.



4. Discussion

HMTD is sufficiently shock sensitive that it has been used as a primary explosive [6]. In contrast triacetone triperoxide TATP, a monocyclic triperoxide is much more stable. While explosive performance is frequently assessed by detonation velocity (4.5 km/s for HMTD and 5.2 km/s for TATP), [2] sensitivity to ignition is judged by a number of tests, a common one is drop mass impact. In the most common form of the drop mass impact test, a 40 mg sample is placed on an anvil and a weight (2 or 5 kg) is dropped on it. A “go” is determined by a loud report; multiple tests are performed [14]. Drop mass impact values for HMTD and TATP are reported as 3 and 10 cm, respectively, [2,15]. These impact stabilities are reflected by their thermal stabilities. For example their first order decomposition rate constants at 150 °C differ by three orders of magnitude [$3 \times 10^{-3} \text{ s}^{-1}$ (HMTD) and

$7 \times 10^{-6} \text{ s}^{-1}$ (TATP)]. The correlation between sensitivity to drop weight and thermal stability has long fascinated those studying energetic materials [16,17]. A classic case is that of 1,3,5-trinitro-2,4,6-triaminobenzene which is well-known for both high thermal stability and high resistance to drop mass impact [18]. Logically, both sensitivities should have their basis in thermal stability. The problem with the correlation, however, is that drop mass and thermal stability are generally examining different temperature regimes [19]. It is not surprising that HMTD should be much more shock sensitive than TATP. HMTD has unusual bond strain with the carbons arranged in exact three-fold coordination about the two bridgehead nitrogen atoms [3,4]. Ring strain provides extra energy to the detonation of energetic materials, but it is probably also a source of enhanced sensitivity, e.g. nitrocubanes [20,21].

An unusual feature of HMTD decomposition was the apparent sudden change in rate and decomposition products that occurred between 150 and 160 °C. In the low temperature regime, thermolyses in air and vacuum gave essentially the same products CO_2 and trimethylamine. At high temperature the principal carbon-containing product was CO not CO_2 ; and trimethylamine was not observed for thermolyses performed in air. At and below 150 °C, the decomposition of HMTD is reasonably first-order. At 160 °C instantaneous decomposition appeared to follow a brief induction period. In examining the decomposition of TATP we considered several possible decomposition mechanisms: concerted loss of O_2 or stepwise decomposition, initiated by O–O homolysis or initiated by C–O homolysis. The experimental results showed the decomposition was stepwise with O–O homolysis the initiating step. The principle products observed were acetone and carbon dioxide, but molecular oxygen could have been formed and subsequently reacted. It was concluded that the same pathway remained dominant over a wide temperature range (150–235 °C) although at high temperatures formation of methyl radical by C–C homolysis became noticeable.

Following decomposition reactions analogous to those proposed for TATP we considered four possible homolytic decomposition routes for HMTD: two concerted; two stepwise; two involving O–O homolysis; and two involving C–O homolysis (Fig. 6). Postulating O–O homolysis (routes (b) and (c)) made

direct formation of trimethylamine difficult to explain. For a bridgehead nitrogen to retain its original methylene groups yet form trimethylamine, $-\text{OCH}_2-\text{NR}_2$ must be transformed to CH_3-NR_2 . If the bridgehead nitrogen does not retain its original methylene groups but forms trimethylamine by gaseous interactions of smaller molecules, it would seem likely that other methylamines (mono and di) would also be formed. However, under none of our experimental conditions were monomethylamine or dimethylamine observed. Both routes (a) and (d) postulate C–O bond cleavage. The unique structure of HMTD may cause C–O cleavage to be favored over the O–O homolysis typical for peroxides. Cleavage of C–O would relieve ring strain and allow straight-forward production of trimethylamine. However, the concerted route (a) undoubtedly would be of high energy and very unlikely. Of the four homolytic routes considered, route (d), loss of molecular oxygen, would appear most reasonable and produce the observed products. However, the ionic decomposition pathway shown in Fig. 7 would also produce the observed products. Peroxides frequently decompose by homolytic O–O cleavage; however, we postulate that is not the case for HMTD. HMTD may be unique in that it may use an ionic decomposition pathway. Certainly at 160 °C there is an abrupt change in rate and reaction products. The change in reaction products can be explained without postulating a change in mechanism, however, the rapid acceleration of decomposition observed may be best explained by a change from an ionic (Fig. 7) to a free radical (Fig. 6d) decomposition route. Labeling studies do not differentiate between these two routes, but use of radical trapping agents might. To date we have not probed the high temperature regime because decomposition is close to instantaneous.

The observed decomposition products at low or high temperatures can be explained without a change in mechanism. As implied by Eq. (2) we believe trimethylamine is formed over the entire temperature range studied (100–180 °C). However, at 160 °C and above, when levels of molecular oxygen were sufficient (possibly after a brief induction period) that the oxygen attacked the amine so that trimethylamine was not observed. Considered as an explosive, HMTD is oxygen deficient, i.e. it does not contain sufficient oxygen to convert all hydrogen atoms to water and all carbon to CO or CO_2 . TATP has a similar deficiency,

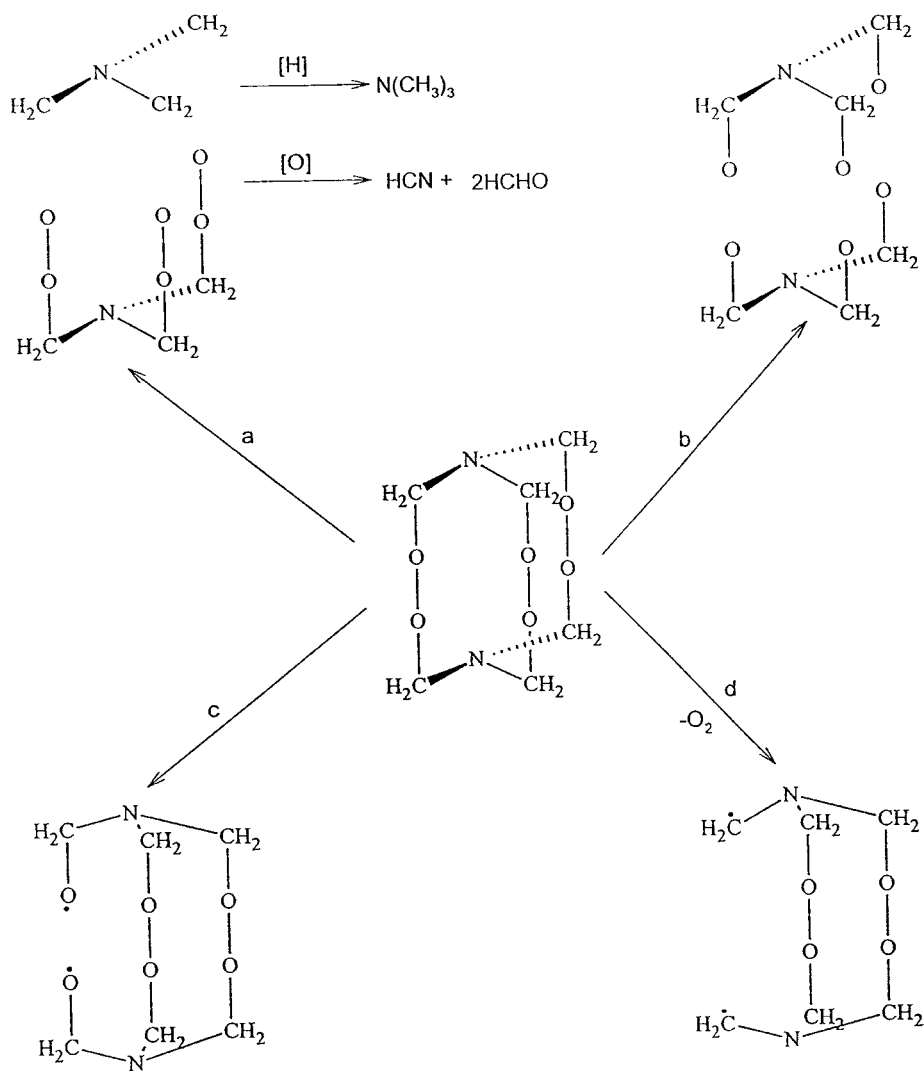


Fig. 6. Possible homolytic decomposition routes of HMTD.

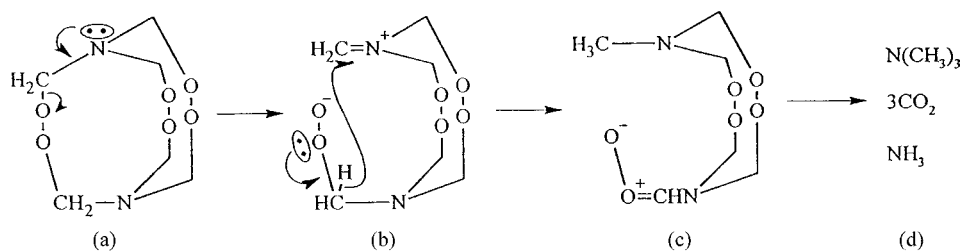


Fig. 7. Proposed ionic decomposition route of HMTD.

but under thermolysis conditions TATP produces acetone, thus, using only one oxygen atom to tie up three carbon and six hydrogen atoms. The low-temperature decomposition of HMTD ties up three carbons and nine hydrogen in trimethylamine; thus, there were sufficient oxygen atoms to convert the remaining three carbons to CO₂ or CO. Under conditions where trimethylamine is oxidized, there is insufficient oxygen. Reaction (2) leaves 0.75 mole of O₂, but for reaction (3) to go to completion another 0.25 mole of molecular oxygen is required. At the normal scale of our experiments, the air-filled reaction tubes provided 0.5–0.7 mole of molecular oxygen per mole HMTD; there was just sufficient oxygen to destroy all trimethylamine. However, under vacuum some trimethylamine survived. Therefore, the change in thermolysis products observed at and above 160 °C can be explained by a secondary reaction (of trimethylamine). However, while an abrupt change in mechanism need not be postulated to explain the change in products, it may explain the dramatic increase in decomposition rate observed at and above 160 °C.

5. Conclusions

The thermal decomposition of HMTD is initiated by a first-order elimination of O₂. The need to eliminate ring strain makes this a relatively low temperature and fast event compared to the decomposition of TATP. Two mechanisms for oxygen elimination have been proposed, ionic and free radical. While experimental data cannot distinguish between them, the rapid increase in decomposition rate observed between 150 and 160 °C suggests the dominant mechanism may switch from ionic to free radical in that temperature range. Subsequent decomposition of the remaining species results in the products CO₂, trimethylamine and ammonia at temperatures of 150 °C or less. Above 150 °C a secondary reaction becomes important, the oxidation of the trimethylamine to HCN and methanol. Due to the increased number of carbons to be oxidized, carbon monoxide rather than carbon dioxide was the major carbonaceous product in the high temperature thermolysis. When oxygen was limited by performing the thermolysis in vacuum, there was insufficient oxygen to oxidize all the trimethylamine and some was observed in the decomposition products.

Acknowledgements

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