Determining the Vapor Pressures of Diacetone Diperoxide (DADP), and Hexamethylene Triperoxide Diamine (HMTD)

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Abstract:

The vapor signature of diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD) were examined by a gas chromatography (GC) headspace technique over the range of 15 to 55°C. Parallel experiments were conducted to re-determine the vapor pressures of 2,4,6-trinitrotoluene (TNT) and triacetone triperoxide (TATP). The TNT and TATP vapor pressures were in agreement with previously reported results. Vapor pressure of DADP was determined to be 17.7 Pa at 25°C, which is approximately 2.6 times higher than TATP at the same temperature. The Clapeyron equation, relating vapor pressure and temperature, was LnP (Pa) = 35.9-9845.1/T (K) for DADP. Heat of sublimation, calculated from the slope of the line for the Clapeyron equation, was 81.9 kJ/mole. HMTD vapor pressure was not determined due to reduced thermal stability resulting in vapor phase decomposition products.

Key Words:

DADP (diacetone diperoxide), HMTD (hexamethylene triperoxide diamine), TATP (triacetone triperoxide), TNT (2,4,6-trinitrotoluene), Vapor pressure of explosives, Explosive detection

Introduction:

The range of military explosives is rather limited due to stringent safety, performance, and stability requirements. However, such considerations do not apply to terrorists. This gives them a larger palette of chemicals from which to choose. Chemicals with multiple peroxide functionalities, such as TATP, DADP and HMTD (Figure 1), are not used by the military due to their high sensitivity to friction, shock and heat.[1-5] Even terrorists usually limit their synthesis of these to a modest scale, using them as initiating explosives, rather than main charges. Due to their ease of preparation they have been used extensively by terrorists in the Middle East and in the July 2005 London bombings. HMTD was one of the materials prepared and carried into the U.S. by the would-be millennium bomber Ahmed Ressam to initiate his intended urea nitrate bombs (Dec. 1999).[6-7]

An important consideration in detection of explosives is their vapor signature. Ideally, such a signature is the molecule, itself, its vapor; but the signature could be a decomposition product or contaminant. We have reported the vapor pressure of TATP to be 6.95 Pa at 25°C[8]; about 10^4 times the vapor pressure of TNT.[9] DADP, a byproduct of TATP synthesis, has a similar structure to TATP (Fig. 1). The lower molecular weight of DADP suggests a higher vapor pressure than TATP. This study reports the vapor pressure of DADP as determined by a gas chromatograph/electron capture detection (GC/ECD) method previously used to determine the vapor pressure of TATP.[8] From the DADP vapor density, vapor pressures were calculated using the ideal gas law (PV=nRT) and the volume of gas injected into the GC (10 μL).[10] Vapor pressure under different temperatures are tested and graphed. The linearity of the graphical results is consistent

with the Clapeyron equation, which suggests that the enthalpy was relatively constant over the temperature range. To verify the validity of these results, the experiments included vapor pressure determinations of TNT and TATP whose results have been previously reported. Both these tests were in agreement with the previous literature.[11-14]

Experimental Section:

Samples of DADP, TATP and HMTD were prepared in our laboratory. TNT was obtained from Battelle Memorial Institute. Samples of DADP, TATP, HMTD, and TNT were sealed in Agilent 10mL headspace, crimp–top, flat-bottom vials with Agilent 20 mm gray butyl headspace vial septa and allowed to equilibrate for at least four days at room temperature. The high performance oven of a Hewlett Packard 5890 GC was used to equilibrate the samples at the desired temperature. After equilibration for at least 2 hours at a specified temperature, a 10μL gas tight syringe (warmed in the oven with the vials) was used to inject 10μL samples into an Agilent 6890N GC equipped with a J&W DB-5 capillary column (30m X 0.25mm X 0.25 um film) and micro-electron capture detector (uECD). Vials of DADP and TATP were placed in the oven at the same time to eliminate the effect of temperature difference. Analysis of the TATP and TNT, whose vapor pressures have been reported, were used to validate the results for DADP and HMTD.

An Agilent 6890 GC with u-ECD and a J&W DB-5 column [30m x 0.25 mm x 0.25 um (film)] was employed for both DADP and TATP. The inlet was set at 165°C with a 125:1 split ratio. The oven temperature started at 50°C, and after a 2 minute hold it was increased to 220°C at a ramp of 20°/minute. The helium flow rate through the

column was held constant at 4.0mL/minute. The u-ECD detector was held at 300°C. Under these conditions, TATP retention time was 5.7 minutes, and DADP retention, 3.0 minutes. For TNT all the GC conditions were the same as above except that the split ratio of the inlet was 5:1 and the final oven temperature was 280°C. The TNT retention time was 9.57 minute. For HMTD, a shorter J&W DB-5 column [6m x 0.53 mm x 1.5 um (film)] was used. The split ratio of the inlet was 5:1; the final oven temperature was 280°C; and the carrier gas was hydrogen. HMTD retention time was 4.43 minutes.

Quantification of the vapors was determined by external standards methods. Calibration standards of DADP, TATP, HMTD and TNT were prepared from acetonitrile standards in the concentration ranges suitable for quantitative analysis of the vapors. Detector linearity was high with the square of the correlation coefficient at least 0.99; (typical calibration curves are shown in Figure 2). In order to determine vapor pressures, it was assumed that the vapors were the molecular species and obeyed the ideal gas law [P= (mRT)/(MV)]. The mass of the chemical (m) was determined from the standard calibration curve. A value of R, the gas constant, 8.314×10^{6} (mL*Pa/mol*K) was used; T is the Kelvin temperature; V is the volume of the gas, which is 0.010mL (10μL syringe used for GC injection); M is the molar mass of the chemicals (DADP=148, TATP=222, TNT=227).

Results and Discussion:

Table 1 lists the vapor pressures of DADP, TATP, and TNT at various temperatures. The TATP results are similar to those previously reported.[8] Over the temperature range from 15°C to 50°C, DADP has a much higher vapor pressure than

TATP; this is probably related to its lower molecular weight. At 25°C, the vapor pressure of DADP is 17.7 Pa and TATP is 7.87 Pa. This corresponds to 7.13×10^{-11} moles of DADP in 10μL compared with 3.15×10^{-11} moles of TATP at 25°C or 2.6 times more DADP than TATP. This suggested that it should be easier to detect DADP than TATP. Vapor pressures of common explosives are given in Table 2.[15] For TNT there are only 6.72×10^{-15} moles, so both DADP and TATP are much more detectable than TNT at 25°C.

The vapor pressure of TNT was first reported around 1950. At that time a Knudson effusion technique was used. In the late 1970's TNT vapor pressure was re-determined using gas chromatography, a technique less sensitive to minor volatile impurities.[13,16] As shown in Table 3 results for TATP and TNT were comparable with previous studies. Literature values are reported for ambient TNT vapor pressure and the dependence of it on temperature. At 25 °C, the literature value of TNT was 6.0×10^{-4} Pa.[17] The vapor pressure calculated in this study, 8.4×10^{-4} Pa, was in good agreement with this value. Our previously reported TATP vapor pressure at 25 °C was 6.95 Pa[8]. The result for TATP in the present study was 7.87 Pa.

The graphs used for determining the Clapeyron equations over the temperature range 15 to 50°C for TATP and DADP are shown in Figure 3. The equations best describing the dependences of DADP and TATP vapor pressures on temperature are Ln P(Pa) = 35.9-9845.1/T(K) and LnP(Pa) = 31.4-8719.9/T, respectively. From the slopes of the graphs the heats of vaporization (sublimation) have been determined to be 81.9kJ/mol (DADP) and 72.5kJ/mol (TATP). Figure 3 contrasts the vapor pressures of DADP, TATP, and TNT. The ambient DADP vapor pressure ~ 17.7 or ~12 ng per 10μL of air is an amount readily observable with modern laboratory instrumentation.

Using the same protocol used to evaluate the vapor pressure of DADP, an attempt was made to determine the vapor pressure of HMTD. While peaks were observed in the GC chromatogram, these appeared to be decomposition products or impurities rather than HMTD. We had previously assessed HMTD thermal decomposition down to 100°C by observing the volume of gas evolved.[18] We extended the range down to 60°C tracking actual HMTD loss (Table 4) and used those kinetics to calculate Arrhenius constants (E = 120 kJ/mol; A = 5.58 x $10^{12}s^{-1}$) and extrapolate HMTD thermal stability down to room temperature (Fig. 4). Its thermal stability is substantially poorer than TATP[19] or DADP[20] (Fig. 5). HMTD is made from the acidified mixture of hexamine and hydrogen peroxide. If the HMTD is not highly purified by re-crystallization, decomposition is even faster. Identified decomposition products are N,N'-dimethylformamide, N,N'-methylenebis(formamide), trimethylamine, and hexamine. These appear to be its "vapor signature."

Conclusions:

The vapor pressure of DADP has been determined at ambient conditions to be 17.7 Pa. Since this vapor pressure is higher than that of TATP and since the synthesis of TATP often results in mixtures with DADP, its signature is an important component of the TATP signature. Such a situation has been observed and exploited in detection of TNT. The higher vapor-pressure dinitrotoluenes which contaminate all TNT have been used to facilitate the detection of the lower vapor pressure TNT. Both TATP and DADP exhibit vapor pressures on the order of that of 2,4-dinitrotoluene, a material readily detectible by explosive detection equipment and canines. In contrast, HMTD has low

volatility, but decomposition products caused by age or impurities give it a pungent, fishy odor with time.

Acknowledgements:

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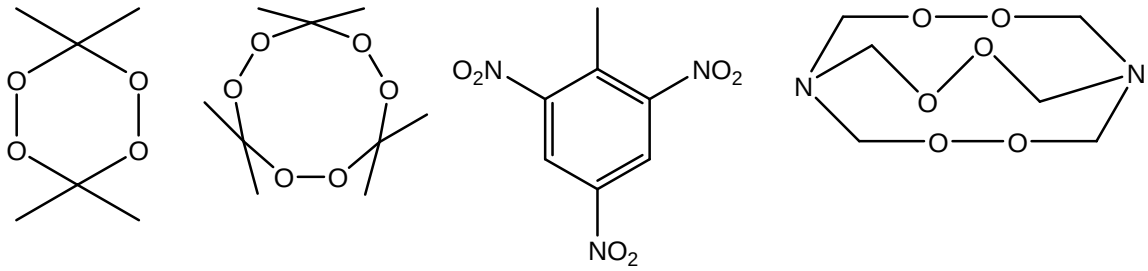
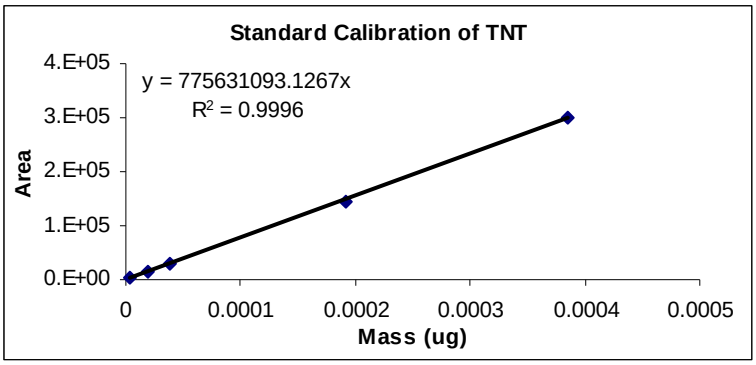
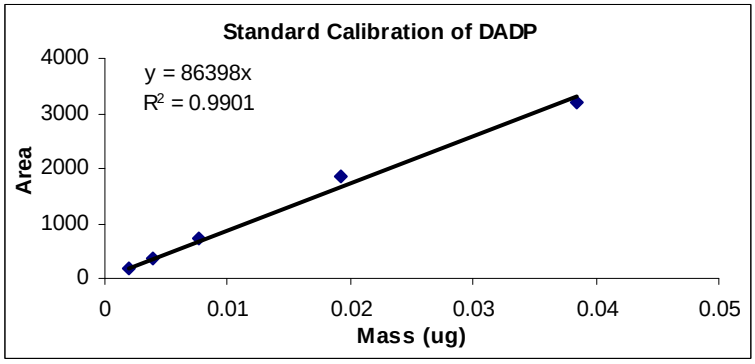
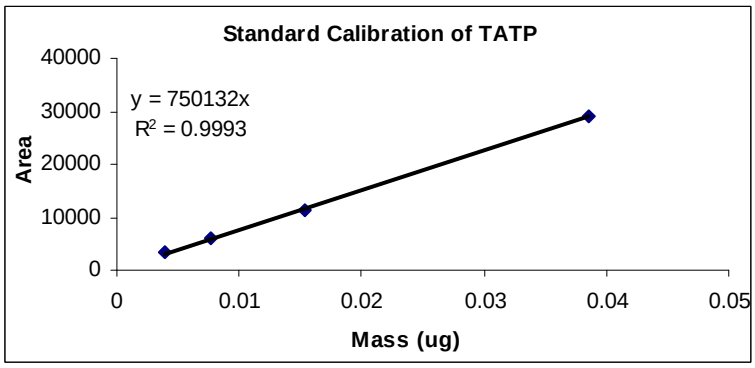


DADP **TATP** **TNT** **HMTD**

Fig. 1. Structures of DADP, TATP, TNT and HMTD







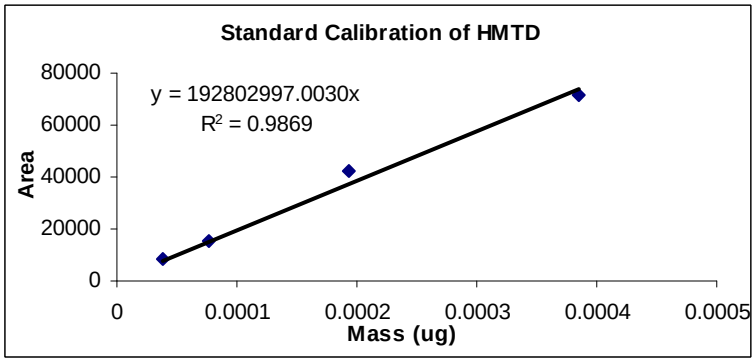


Fig. 2 Standard Calibration of DADP, TATP, HMTD and TNT

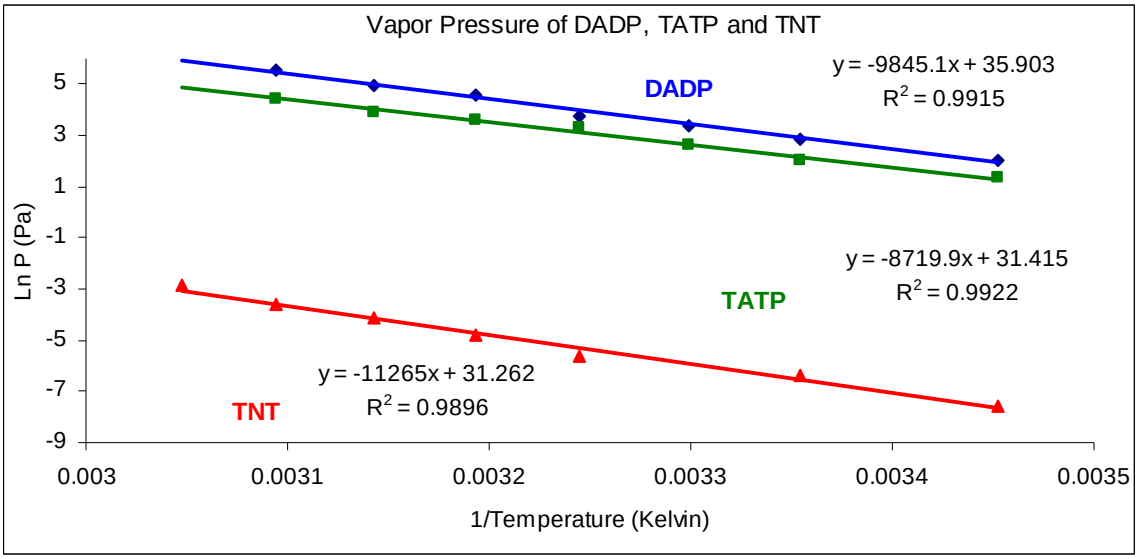


Fig. 3. Clapeyron Equation of DADP, TATP, & TNT

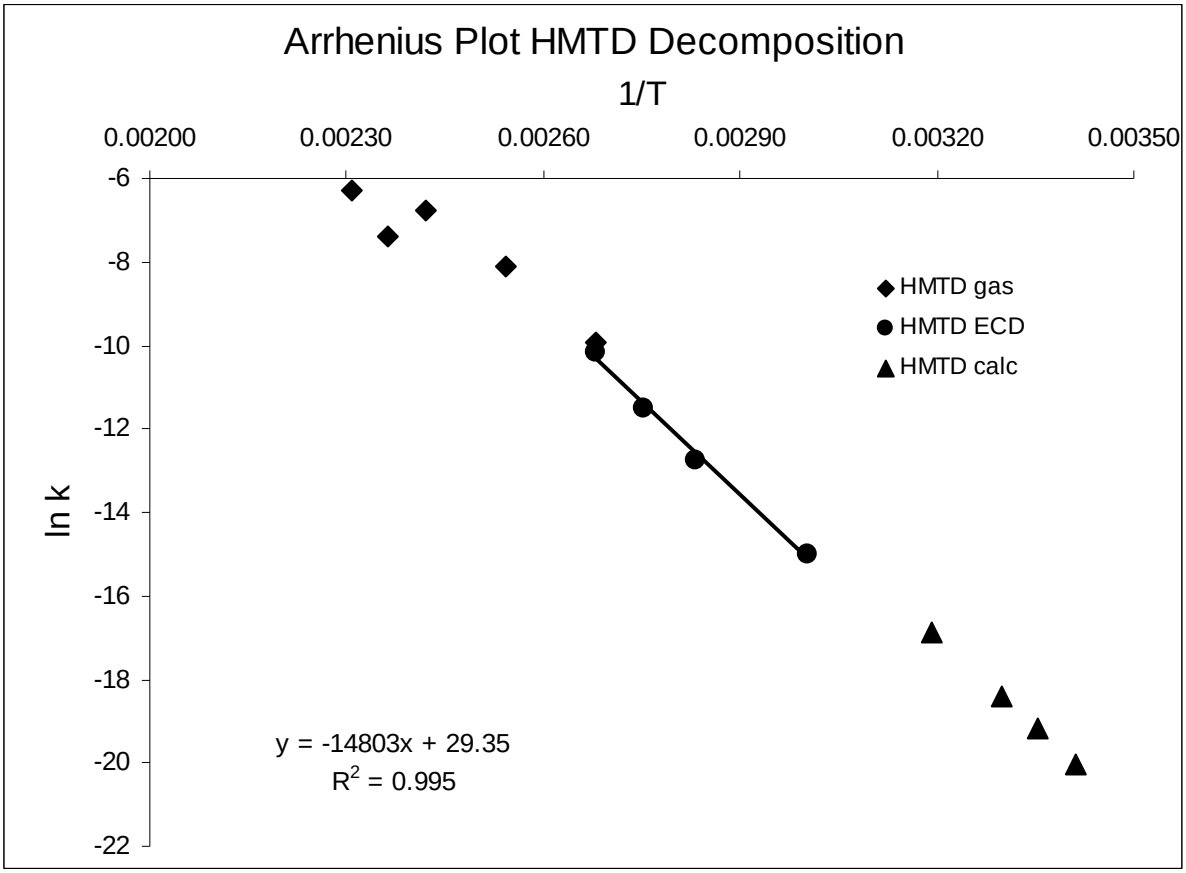


Fig. 4: Arrhenius Plot of HMTD Decomposition

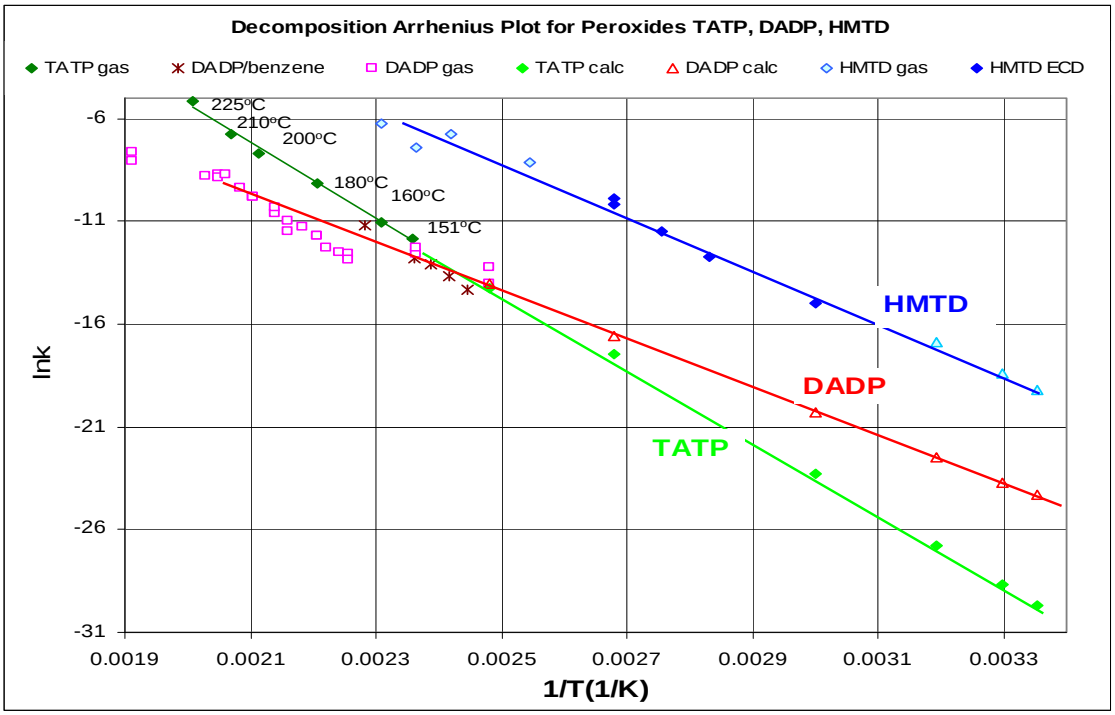


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Table 1. Vapor pressures at different temperatures for DADP, TATP, and TNT

Temperature		DADP		TATP		TNT	
(^{o}C)	(K)	P (Pa)	ug in 10 uL	P (Pa)	ug in 10 uL	P (Pa)	ug in 10 uL
15	288	7.47	4.61E-03	3.73	3.46E-03	5.33E-04	5.06E-07
25	298	17.33	1.04E-02	7.87	7.05E-03	1.73E-03	1.59E-06
25	298	17.73	1.06E-02	8.40	7.53E-03	1.73E-03	1.59E-06
25	298	18.13	1.08E-02	7.20	6.45E-03	1.73E-03	1.59E-06
30	303	29.33	1.72E-02	14.13	1.25E-02	--	--
35	308	42.26	2.44E-02	26.93	2.33E-02	3.73E-03	3.31E-06
40	313	95.19	5.41E-02	35.86	3.06E-02	8.40E-03	7.33E-06
45	318	137.45	7.69E-02	49.46	4.15E-02	1.60E-02	1.37E-05
50	323	255.58	1.41E-01	84.93	7.02E-02	2.67E-02	2.25E-05
55	328	--	--	--	--	5.73E-02	4.77E-05

Table 2. Properties of Some Explosives

Explosive	MW	m.p.	T_{exp}	vapor pressure (Pa)			
	g mol^{-1}	^oC	^oC	20^oC	Ref.	100^oC	Ref.
EGDN	152	liquid	237	5.1	15	2600	14
NG	227	13	270	0.033	15	55	15 calc.
TATP	222	94	227*	2.0	8	31000	8
2,4-DNT	182	69	270	0.99	11	3800	11 calc.
TNT	227	81	288	1.6E-4	10	14.32	15
PETN	316	141	210	8E-4	12	0.12	12 calc.
RDX	222	204 d	217	4E-7	12	0.012	12 calc.

* DSC exothermic maximum at 20° per minute

Table 3. Literature Values for DADP, TATP and TNT Vapor Pressure

Values for DADP, TATP & TNT Vapor Pressure					
$Log_{10}P(mmHg) = A-[B/T(K)]$					
A	B	mm Hg at 25°C	Pa at 25°C	ΔH_{sub} (kJ/mol)	TNT Reference #
3.35	2562	5.62E-06	7.50E-04	113	15
8.754	4227	3.94E-6	5.25E-04	81	14
15.43	6180	4.92E-06	6.56E-04	118	11
12.31	5175	8.79E-06	1.17E-03	--	13
19.23	7371	3.08E-06	4.11E-04	--	12
17.666	5708	5.21E-02	6.93	109	TATP – 8
10.92	4723	1.30E-5	1.71E-3	91	TNT --this work
11.52	3787	5.90E-02	7.85	73	TATP --this work
13.467	4275	1.33E-01	17.89	81	DADP--this work

Table 4: HMTD Decomposition Rate Constants

Temp (^{o}C)	k s^{-1}	experiment	reference
60	3.10E-07	GC-MS	this work
80	2.96E-06	GC-MS	this work
90	1.03E-05	GC-MS	this work
100	3.82E-05	GC-MS	this work
100	4.96E-05	gas manometry	ref 19
120	2.96E-04	gas manometry	ref 19
140	1.14E-03	gas manometry	ref 19
150	6.27E-04	gas manometry	ref 19
160	1.90E-03	gas manometry	ref 19