

Determination of the Vapor Density of Triacetone Triperoxide (TATP) Using A Gas Chromatography Headspace Technique

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Key Words

TATP

1,1,4,4,7,7-hexamethyl-1,4,7-cyclonona-triperoxane

TNT

2,4,6-Trinitrotoluene

Vapor pressure of explosives

Explosive detection

Summary

Using a GC headspace measurement technique, the vapor pressure of TATP was determined over the temperature range 12 to 60°C. As a check on the experimental method, TNT vapor pressure was likewise computed. Values for TNT are in excellent agreement with previous published ones. For TATP the vapor pressure was found to be ~0.05 mm Hg at ambient conditions. This value translates to a factor of 10^4 more molecules of TATP in air than TNT at room temperature. The dependence of TATP vapor pressure on temperature can be described by the equation $\log_{10}P(\text{mm Hg}) = 17.666 - 5708/T(\text{K})$. Its heat of sublimation has been calculated as 109 kJ/mol.

1 Introduction

TATP (triacetone triperoxide or 1,1,4,4,7,7-hexamethyl-1,4,7-cyclonona-triperioxane), with multiple peroxide functionality, is better oxygen balanced than most commercial peroxides (Fig. 1). Because of extreme sensitivity to shock and overall exothermic decomposition, it requires special precautions when handling.^{1,2} Despite these limitations, recently it has found use as an improvised explosive because synthesis, using easily obtainable materials, is straightforward.³⁻⁸

Detection of explosives by certain instrumentation and by canines is dependent on the vapor pressures of the materials.⁹ This study used gas chromatography with electron capture detection (GC/ECD) to obtain the vapor density of TATP in sealed sample vials containing the crystalline material. From the TATP vapor densities, vapor pressures were calculated using the ideal gas law and the volume of gas (10 μ L) introduced into the GC injector.¹⁰ The linearity of the graphical results of natural logarithm of vapor pressure versus reciprocal of Kelvin temperature

are consistent with the Clapeyron equation, suggesting that enthalpy of vaporization (ΔH_{vap}) was relatively constant over the temperature range studied. To verify the validity of our technique, the experiment was repeated for 2,4,6-trinitrotoluene (TNT). The TNT results were in good agreement with the literature.¹⁰⁻¹⁴

2 Experimental Section

2.1 Preparation of 1,1,4,4,7,7-Hexamethyl-1,47-cyclononatriperoxane (triacetone triperoxide or TATP)

The following is a modification of a method developed by Milas.¹⁵ Into a setup comprising a stir plate and liquid bath of 50/50 mix water/ethylene glycol at -20°C was placed a 100ml round bottom flask with magnetic stir bar. A mixture of 8 ml (14.72 g, 0.15 mol) H_2SO_4 and 10 ml acetone was added dropwise by automated means over 1 h to a stirred solution of 10 ml (7.86 g, 0.135 mol) acetone and 8.5 ml (9.35 g, 0.135 mol) 50% v/v hydrogen peroxide solution. The reaction kept as cold as possible taking care to not allow the solution to become frozen. After addition of the acid was complete, the reaction was allowed to stir for an additional 1 h at near -5°C . The reaction was then removed from the bath, 25 ml of CH_2Cl_2 was added, and the solution was warmed to room temperature. The product was extracted with CH_2Cl_2 and washed free of acid with water. About 75% of the solvent was evaporated. The remaining solution was put in the freezer overnight. The resulting crystals were filtered and re-crystallized in methanol, yielding good purity clear colorless crystals 6.383g (yield 64 %).

Crystallization straight from the reaction mixture can be performed by allowing the mixture to stand in the freezer overnight, filtering and thorough washing of the resulting crystals with water. However, to insure stability, re-crystallization from methanol must be performed. melting point: $93-98^{\circ}\text{C}$; NMR shift (^1H in DMSO-D_6) CH_3 δ 1.36. **WARNING:** TATP can act

as a primary explosive. It should only be prepared in small batches by properly trained personnel with precautions against blast. The material is best stored below room temperature.

2.2 Vapor Pressure Determination

Samples of TNT and TATP were sealed in Agilent 10 ml headspace crimp top flat bottom vials with Agilent 20 mm gray butyl headspace vial septa and allowed to equilibrate for at least four days. An oven of a Hewlett Packard 5890 GC was used to equilibrate the samples at various temperatures. After equilibration at a given temperature for at least two hours, 10 μ L samples were injected onto a Agilent 6890N GC equipped with a HP-5 capillary column (30m X 0.32mm X 0.25 μ m film) and micro electron capture detector. For TNT and TATP the GC conditions were as follows:

Inlet: Temp. 165 $^{\circ}$ C; Split Mode 125:1 (TATP) or 5:1 (TNT); Constant Flow

Oven: Initial Temperature 50 $^{\circ}$ C; Initial Hold Time 2 min; Ramp 20 $^{\circ}$ C/min; Final Temperature 280 $^{\circ}$ C; Final Hold Time 2 min

Detector: micro-ECD; Temperature 300 $^{\circ}$ C

Carrier Gas: Helium

TNT and TATP calibration curves were prepared from acetonitrile standards in the concentration ranges suitable for quantitative analysis of their respective head space vapors. Typical calibration curves (peak area versus μ g TATP or TNT) are given in Figure 2 for TATP and Figure 3 for TNT. Linearity, as expressed by the square of the correlation coefficient, exceeded 0.99 for all calibration curves. The GC was used to determine the μ g of TATP or TNT in fixed volumes (10 μ L) of headspace gas. The volume of gas was withdrawn through the septum of the equilibrated headspace vials using a 10 μ L gas tight syringe. It was assumed that the TATP and TNT vapor obeyed the ideal gas law [$pV = (m/M)RT$] where $m = \mu$ g TNT or TATP; $M =$ molar mass TNT ($227 \times 10^6 \mu$ g/mole); or TATP ($222 \times 10^6 \mu$ g/mole); $R =$ gas constant = $6.236 \times 10^4 \text{ ml}\cdot\text{mm Hg/mol}\cdot\text{K}$; $T =$ temperature kelvin; $V =$ volume (0.010 ml).

Using the preceding values in the specified units and solving for P yielded the vapor pressure of TATP or TNT in units of mm Hg.

3 Results & Discussion

The micrograms of TATP and TNT in 10 μL of headspace and the calculated headspace vapor pressures (in mm Hg) of TATP and TNT are given in Table 1 over a fifty degree temperature range. Although TATP and TNT have similar molar masses (222 g mol^{-1} versus 227 g mol^{-1}), TATP is considerably more volatile than TNT. At 25°C there is about 6 ng of TATP in 10 μL of air. This corresponds to about 3×10^{-11} moles or about 1.7×10^{13} TATP molecules in 10 μL . By contrast, at 25°C , about 5×10^{-4} ng of TNT in 10 μL corresponds to $\sim 2 \times 10^{-15}$ moles or 1.3×10^9 TNT molecules. There are about 13000 times as many molecules of TATP than TNT in the headspace at 25°C .

The vapor pressure of TNT was first reported around 1950; at that time a Knudson effusion technique was used.¹⁰ In the late 1970's TNT vapor pressure was re-determined using gas chromatography, a technique less sensitive to minor volatile impurities.^{11,12} We determine TNT vapor pressure herein as a check on our technique. Table 2 shows literature values reported for ambient TNT vapor pressure and the dependence of it on temperature. The vapor pressure calculated in this study, 4×10^{-6} mm Hg, is in excellent agreement with these literature values. Furthermore, the heat of sublimation (ΔH_{sub}), calculated from the Clapeyron relationship (eq 1) is also in good agreement with previously determined heats of sublimation.

$$d\ln P/d(1/T) = -\Delta H_{\text{sub}}/R \quad (1)$$

Since our experimental approach produces the agreed values for ambient vapor pressure and heat of sublimation for TNT, it should also correctly represent the ambient vapor pressure of

TATP. This study showed that the equation best describing the dependence of TATP vapor pressure on temperature is

$$\log_{10}P(\text{mm Hg}) = 17.666 - 5708/T(\text{K}).$$

Figure 4 contrasts the vapor pressures of TATP and TNT over the temperature range 12 to 60°C.

The ambient TATP vapor pressure ~ 0.05 mm Hg or ~6 ng per 10 μL of air is an amount readily observable with modern laboratory instrumentation. Computing heat of sublimation as above, we find ΔH_{sub} equal to 109 kJ/mol.

Among military explosives TNT is quite volatile, making its detection relatively easy (Table 3). Practical experience indicates TATP is much more volatile than TNT. While TNT will undergo noticeable sublimation upon heating, TATP undergoes substantial sublimation at ambient conditions.¹⁶ This observation is in line with the data reported herein. The vapor pressure of TATP is about 13000 times that of TNT. Surprisingly, the heats of sublimation of the two substances are nearly the same. The fact that TATP has a vapor pressure four orders of magnitude larger than TNT and the fact that its parent ion can be detected by GC/MS suggest that it should be extremely easy to detect. Indeed, both the Forensic Explosive Lab of the Defense Science and Technology Laboratory and our laboratory at University of Rhode Island have successfully prepared canine training aids simply by suspending gauze or cotton balls in a closed container of TATP.^{17,18}

5 Conclusions

The vapor pressure of TATP has been determined at ambient conditions to be 0.05 mm Hg. This value is orders of magnitude higher than that of TNT. TNT is an explosive readily

detectible by a variety of explosive detection instrumentation as well as by canines. This study indicates that, barring difficulties in handling, TATP should be even more readily detected.

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Table 1. Vapor Pressures versus Temperature for TATP and TNT.

Temperature		TATP			TNT		
(°C)	(K)	µg in 10 µL	Vapor Pressure (mm Hg)	Vapor Pressure (Pa)	µg in 10 µL	Vapor Pressure (mm Hg)	Vapor Pressure (Pa)
12	285	8.87E-04	7.11E-03	0.95	1.58E-08	1.24E-07	1.65E-05
12	285	1.06E-03	8.50E-03	1.13	1.87E-08	1.46E-07	1.95E-05
21.5	294.5				2.12E-07	1.72E-06	2.29E-04
21.5	294.5				2.06E-07	1.67E-06	2.23E-04
22	295	1.68E-03	1.39E-02	1.85			
22	295	1.30E-03	1.08E-02	1.44			
25	298	6.22E-03	5.21E-02	6.95	4.92E-07	4.03E-06	5.37E-04
25	298	6.22E-03	5.21E-02	6.94	4.43E-07	3.63E-06	4.84E-04
25	298	6.22E-03	5.21E-02	6.94	4.60E-07	3.77E-06	5.03E-04
25	298	6.22E-03	5.21E-02	6.95	4.85E-07	3.97E-06	5.29E-04
25	298	6.14E-03	5.14E-02	6.86	4.85E-07	3.97E-06	5.29E-04
25	298				4.85E-07	3.97E-06	5.29E-04
25	298				5.10E-07	4.18E-06	5.57E-04
25	298				4.92E-07	4.03E-06	5.37E-04
30	303				9.21E-07	7.67E-06	1.02E-03
30	303				9.68E-07	8.06E-06	1.07E-03
32	305	1.47E-02	0.126	16.8			
32	305	1.66E-02	0.142	18.9			
35	308				2.84E-06	2.41E-05	3.21E-03
35	308				2.84E-06	2.40E-05	3.20E-03
40	313				4.78E-06	4.11E-05	5.48E-03
40	313				4.83E-06	4.15E-05	5.53E-03
42	315	3.91E-02	0.346	46.1			
42	315	4.34E-02	0.384	51.2			
45	318				6.75E-06	5.90E-05	7.87E-03
45	318				6.73E-06	5.99E-05	7.99E-03
52	325	8.08E-01	0.738	98.4			
52	325	8.30E-02	0.758	101			
58	331	5.81E-01	5.4	720			
58	331	4.80E-01	4.47	596			

Table 2. Literature Values for TNT and TATP Vapor Pressure

Values for TNT & TATP Vapor Pressure					
$\log_{10}P(\text{mmHg}) = A - [B/T(\text{K})]$				$\Delta H_{\text{sub}} (\text{kJ/mol})$	TNT Reference
A	B	mm Hg at 25°C	Pa at 25°C		
3.35	2562	5.62E-06	7.50E-04	113	14
--	--	5.80E-06	7.73E-04	--	13
15.43	6180	4.92E-06	6.56E-04	118	10
12.31	5175	8.79E-06	1.17E-03	--	12
19.23	7371	3.08E-06	4.11E-04	--	11
8.754	4227	3.94E-06	5.25E-04	81	TNT--this work
17.666	5708	3.25E-02	4.33	109	TATP--this work

Table 3. Properties of Some Explosives

Explosive	MW g mol ⁻¹	m.p. °C	T _{exp} °C	vapor pressure (Pa)			
				20°C	Ref.	100°C	Ref.
EGDN	152	liquid	237	5.1	21	2300	20 calc
NG	227	13	270	0.03-0.2	21,20	55.00	20 calc
TATP	222	94	227*	0.4	this work	31000	this work, calc
2,4-DNT	182	69	270	2.5	22	5 to	
TNT	227	81	288	0.001	calc	15	19,21
PETN	316	141	210	1 to 8 E-06	19, 13 calc	9E-04	19 calc
RDX	222	204d	217	1 to 4 E-07	19,13 calc	9E-05	19 calc

* DSC exothermic maximum at 20° per minute

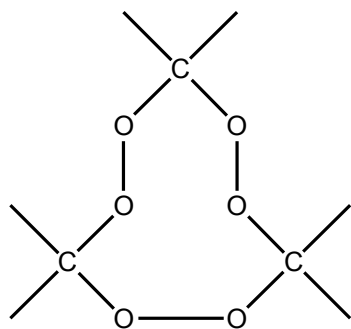


Figure 1. Chemical Structure of TATP

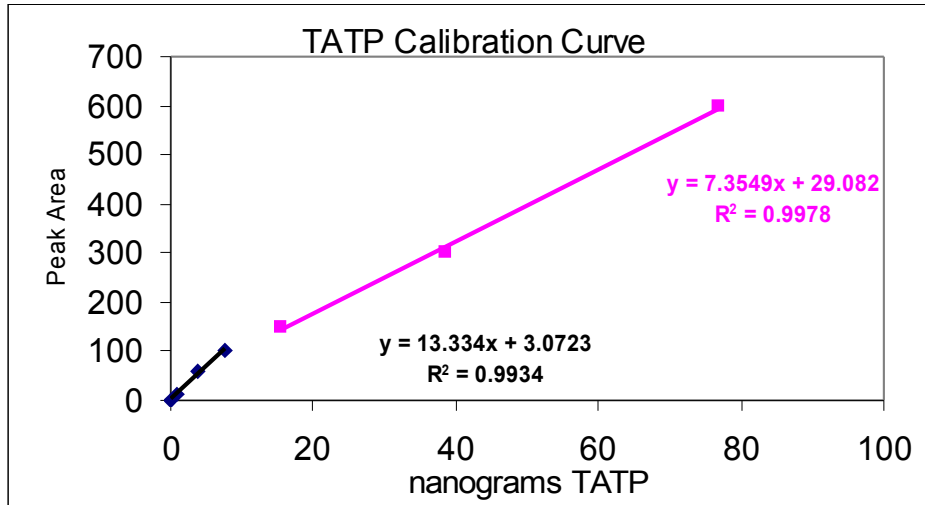


Figure 2. GC Calibration Curve for TATP

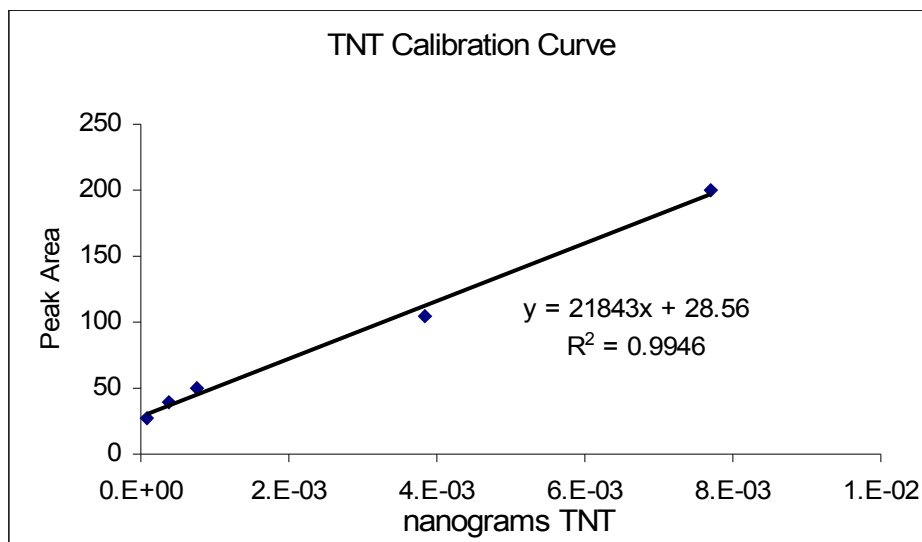


Figure 3. GC Calibration Curve for TNT

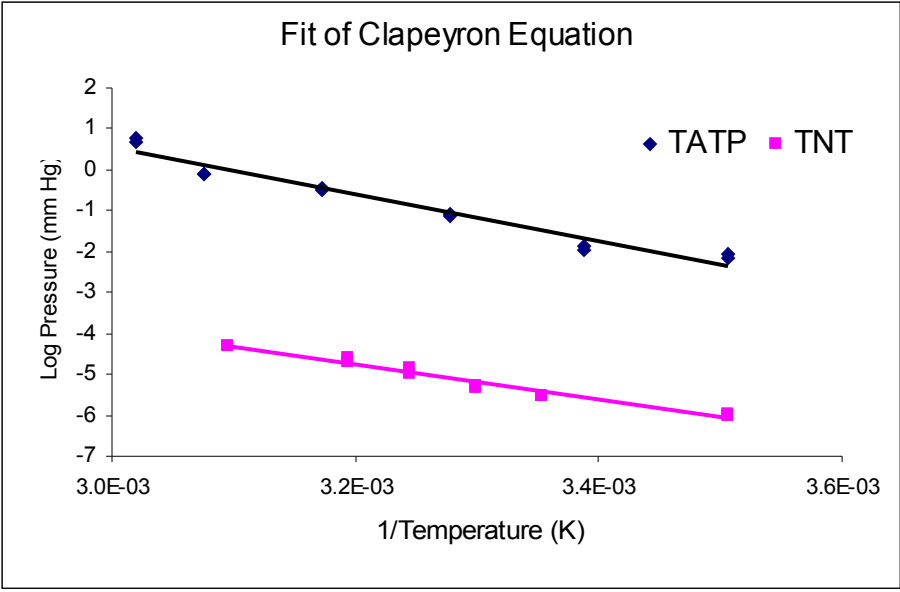


Figure 4 Fit of Clapeyron Equation for TATP and TNT (Linear Fit Values in Table 3)