Vapor Pressure and Heat of Sublimation of Three Nitrotoluenes

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The heat of sublimation of 4-mono-, 2,4-di-, and 2,4,6-trinitrotoluene was calculated from vapor pressure measurements obtained by the Knudsen effusion method. The effect of the nitro group on the parent molecule is estimated. The results are compared with literature values. Equations relating vapor pressure and temperature are presented.

THE nitro group is extremely important in propellant and explosive chemistry. To isolate the effect of this group on the thermodynamic properties of the parent molecule requires corrections to the gaseous state. The heat of sublimation of TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), and PNT (*p*-nitrotoluene) was therefore determined. The choice of the latter two compounds in this study is based on their similarity to TNT in both the position of the NO_2 group and the physical state.

EXPERIMENTAL

Apparatus. The apparatus is based on the Knudsen effusion method (*3, 7*). A 1-inch-diameter brass cup, approximately 0.75 inch in depth, is filled with enough sample just to cover the bottom of the cup. A 1-mil brass foil sheet having a 1-mm-diameter hole is soldered to the top of the cup. (The loss of weight of solder was determined a minimum of 10° above the highest temperature used in the experiments and found to be nil.)

The cup with the sample is placed in an evacuated brass-to-glass sealed chamber. When immersed in a well stirred silicone oil bath, the sample cup is at least 4 inches below the surface of the bath. The lower brass portion assures good thermal contact between the bath and the sample cup. A metal reflector placed 3 inches above the sample cup acts as a radiation shield and helps maintain the same temperature above the sample cup as in the bath.

The temperature of the bath is controlled to better than ±0.005° C. All temperature measurements are made with an NBS-calibrated mercury-glass thermometer, and the usual emergent stem and other corrections are incorporated in the final reading. The thermometer was checked against an NBS-calibrated platinum resistance thermometer and Mueller resistance bridge.

The pumping system provides a vacuum of better than 1×10^{-6} torr. Sample weight loss is measured to ±0.02 mg.

Calibration of Hole Area. The area of the hole, which with the temperature of the sample are two of the most critical factors in this type of experiment, was estimated by two methods.

A. By measuring the vapor pressure of benzoic acid at fixed temperatures and correcting the hole area from the ratio of our measurements to vapor pressure measurements made by both the air transpiration and effusion methods (*2, 3*).

B. Direct measurements of an enlarged photograph taken under a microscope. The area was calculated both from the direct measurement of the hole diameter and by cutting out and weighing a superimposed piece of vellum placed over the hole on the photograph.

Both methods give the same results.

Samples. The mono- and dinitrotoluene are Eastman Kodak products. The TNT was synthesized at Picatinny Arsenal. Table I is a descriptive summary of the sample purity.

The benzoic acid used for determining the area of the hole is a calorimetric standard obtained from the National Bureau of Standards, 39H.

RESULTS

A least-squares equation relating the vapor pressure and temperature is calculated for each compound. The heat and entropy of vaporization are obtained from these equations (Figures 1 to 3). Error is estimated using the correlation coefficient:

$$r = \frac{\Sigma(X_i - \bar{X})(Y_i - \bar{Y})}{[\Sigma(X_i - \bar{X})^2(Y_i - \bar{Y})^2]^{1/2}} \tag{1}$$

The agreement between the observed and calculated values for each sample is good; r = 0.9974, 0.9971, and 0.9835 for TNT, DNT, and PNT, respectively. The experimental data are listed in Table II.

There are three sets of data for the TNT (Figure 1). The circles represent measurements obtained from an estimation of the hole area based on benzoic acid.

Figures 2 and 3 are self-explanatory.

Table I. Sample Purity

Compound	Recrys-tallized from	M.P., °C (Obsd)	X-Ray Impurities	% Carbon Based on Carbon Dioxide	M.P., °C (*8*)
TNT	Benzene	81.1	None	99.86	82
2,4-DNT	Acetone	71.1	None	99.62	70–71
PNT	Acetone	51.5	None	99.70	51.7

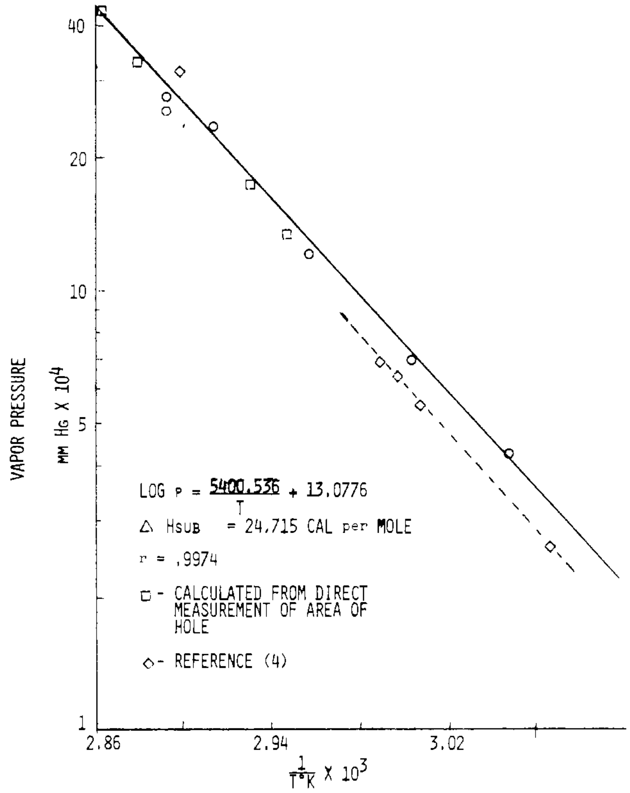

Figure 1. Vapor pressure of trinitrotoluene

DISCUSSION OF RESULTS

Vapor pressure data for 2,4,6-trinitrotoluene have been reported by Edwards (*4*). These data yield a heat of sublimation of 28.3 kcal per mole, compared to our 24.7 kcal per mole. The experimental points from (*4*) which fall in the temperature range are plotted with our data in Figure 1. Four of the five points fall parallel to and below our own measurements. The fifth point, which is several degrees in temperature removed, lies above our measurements.

Two factors make the previous data suspect, sample purity and experimental temperature. The former is not specified. The temperature is not measured directly, but is based on a constant boiling liquid which vaporizes and recondenses around the evacuated chamber. The chamber appears to be made of glass. Possibly the lower thermal conductivity of the glass precludes rapid attainment of the equilibrium temperature between the constant boiling liquid and the sample container.

The calculation of the effect of the NO_2 group on the parent molecule (toluene) is hampered by the lack of ΔC^{s}_{pv} data to 0° K, the preferred reference temperature. A reference temperature of 25° C is chosen in this study because it is the standard for all combustion work. In view of the similarity of the required correction for each of the compounds, a comparison at this temperature is a valid approximation. Corrections for ΔC^{s}_{pv} for TNT and DNT is 8 cal per mole-° K (*1*). As the vapor pressure for each of these compounds was determined down to approximately 35° C, we estimate a correction for ΔC^{s}_{pv} of approximately 0.3 kcal for each. PNT, which was tested at ambient temperature, requires no correction. ΔH_{sub} for toluene is calculated from data listed by Rossini *et al.* (*6*). ΔH_{vap} at 25° C is 9.08 kcal per mole, and ΔH_{fus} at the melting point (−94° C) is 1.582 kcal per mole. ΔH_{fus} is corrected to 25° C by assuming that $\Delta C^{1}_{pv} = 1.5R$.

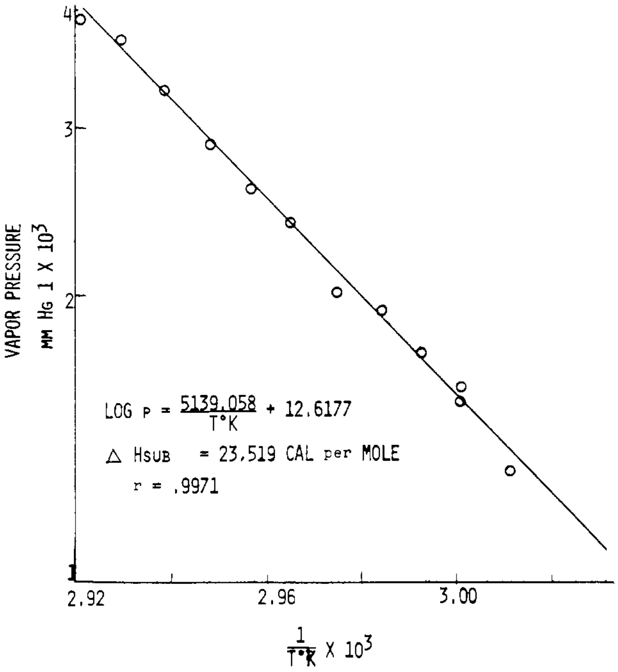

Figure 2. Vapor pressure of 2,4-dinitrotoluene

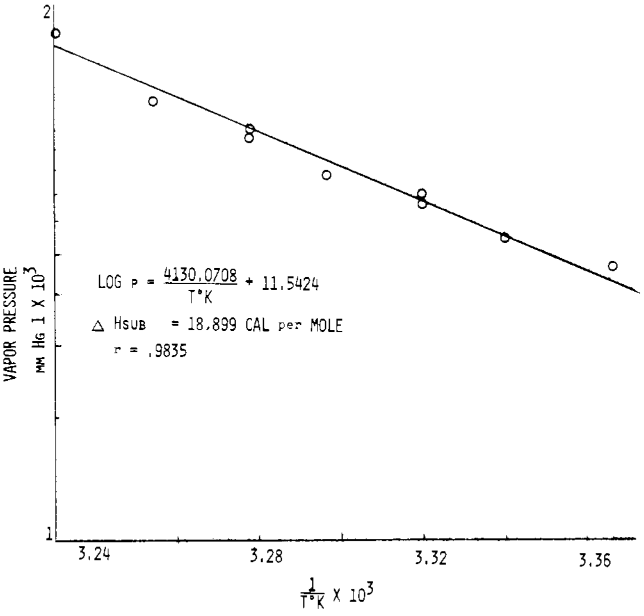

Figure 3. Vapor pressure of *p*-nitrotoluene

The magnitude of the effect of the NO_2 group decreases with increasing substitution (Table III). The increase in ΔH_{sub} *vs.* the number of NO_2 groups is shown in Figure 4. The linearity of the curve may be misleading; the other nitrotoluenes (mono-, di-, and tri-) may not fall on this line.

There are several compilations in which the effect of the NO_2 group on the energy and entropy of sublimation is estimated (*1, 5*). The contribution of an NO_2 group to the heat of sublimation of an aliphatic compound is estimated at 9.6 kcal per mole (*1*) (based on one observation). The contribution per group in tetranitromethane is only 3.26 kcal per mole. The decreasing effect of

Table II. Vapor Pressure of Samples

Temp., °K (Corr.)	Weight Loss, G	Effusion Time, Sec	Pressure, Mm Hg × 10^{-3}
	TNT, M.W. 227.13		
327.906	0.00140	16,200	0.426
332.854	0.00315	22,080	0.701
338.003	0.00540	23,400	1.210
343.170	0.01100	23,460	2.339
345.619	0.01300	23,100	2.749
345.643	0.01180	23,100	2.557
348.215	0.01865	24,300	3.857
339.060[a]	0.00550	12,300	1.358
341.081	0.00450	7,800	1.757
347.131	0.01337	12,300	3.340
349.207	0.01100	7,800	4.347
	2,4-DNT, M.W. 182.14		
331.915	0.01450	5,970	1.298
333.077	0.01525	5,250	1.555
333.077	0.00800	2,670	1.604
334.033	0.01065	3,270	1.746
334.976	0.01065	2,970	1.926
335.974	0.01000	2,670	2.014
337.152	0.01320	2,970	2.394
338.265	0.01425	2,970	2.588
339.063	0.01422	2,670	2.877
340.173	0.01803	2,970	3.285
341.250	0.02035	2,970	3.714
342.277	0.02135	2,970	3.902
	PNT, M.W. 137.14		
297.036	0.01890	2,370	4.663
297.038	0.01910	2,370	4.713
299.192	0.01660	1,770	5.484
299.210	0.01100	1,170	5.498
301.179	0.01410	1,170	7.070
301.215	0.02035	1,770	6.746
303.355	0.01305	990	7.762
303.357	0.11910	8,970	7.818
305.162	0.01975	1,170	9.969
305.183	0.01435	870	9.741
307.310	0.02470	1,170	12.512
307.315	0.02510	1,170	12.714
309.498	0.03440	1,170	17.486
309.508	0.03370	1,170	17.131
309.518	0.04280	1,470	17.317

[a] Hole areas for these four results measured directly. Area = 6.898 × 10^{-3} cm². All other measurements based on hole area determined from vapor pressure of benzoic acid using a different cover. Area = 4.330 × 10^{-3} cm².

Pressure calculated from equation: $p = \frac{g}{AT} \div \left(\frac{M}{2\pi RT}\right)^{1/2}$

Table III. NO_2 Group Contribution

Compound	ΔH_{sub}, Kcal/Mole (25° C)	ΔH per NO_2
Toluene	10.3	. . .
PNT	18.9	8.6
DNT	23.8	6.7
TNT	25.0	4.9

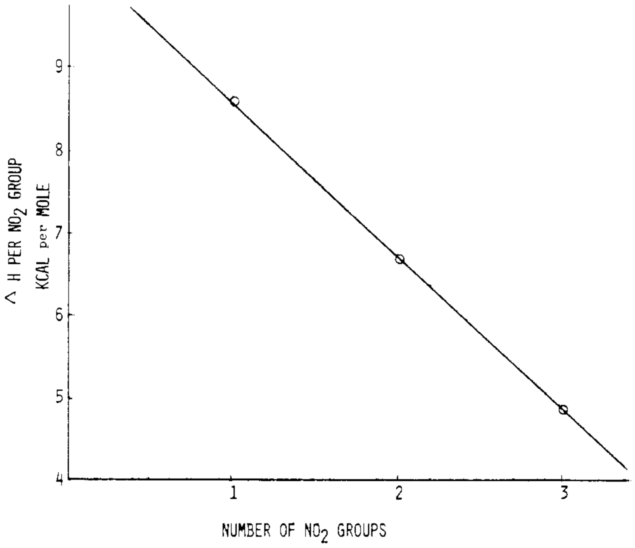

Figure 4. Effect of NO_2 group on heat of sublimation

the nitro group in multiple substitutions is also found in the aromatic compounds (*1*). A single NO_2 group increases ΔH_{sub} by 6.8 kcal per mole; for a dinitro compound two estimates are listed, 5.9 and 5.2 kcal per mole. A trinitro substitution causes a 5.3 kcal per mole contribution. Although the same trend is shown in the literature as reported here, all literature values are based either on a single compound or on measurements which are at best only approximate.

Evidently the substitution of more than one NO_2 group per toluene molecule is not incrementally additive. This is undoubtedly due to the high polarity of the NO_2 group and its influence on inter- and intramolecular forces.

NOMENCLATURE

A = area of hole, cm²
C_p = heat capacity at constant pressure, cal/mole-° K
ΔC_{pv}^{l} = C_p (liquid) − C_p (vapor), cal/mole-° K
ΔC_{pv}^{s} = C_p (solid) − C_p (vapor), cal/mole-° K
ΔH_{sub} = heat of sublimation
ΔH_{fus} = heat of fusion
0° C = 273.15° K
p = pressure
r ± correlation coefficient
R = (gas constant) = 8.3143 × 10^{-7} erg/° K mole and 1.987 cal/mole-°K
$\hat{X}$ = X coordinate from least squares equation
X_i = actual measurement
$\hat{Y}$ = Y coordinate from least squares equation
Y_i = actual measurement

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