CHROM. 9731

VAPOR PRESSURE OF 2,4,6-TRINITROTOLUENE BY A GAS CHROMATOGRAPHIC HEADSPACE TECHNIQUE

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(Received August 9th, 1976)

SUMMARY

The vapor pressure of 2,4,6-trinitrotoluene was determined by a gas chromatographic headspace technique. The vapor pressure from 12–40 °C was derived from the experimental data using the ideal gas law and then compared to extrapolations of literature data obtained by the Knudsen effusion technique. Excellent agreement was obtained. Advantages of the chromatographic headspace method over the effusion method were: (1) scrupulous purity was found to be unnecessary since volatile impurities were chromatographically separated from the compound of interest, (2) the method was sensitive, to less than 10^{-7} torr, using an electron capture detector, and (3) the method was experimentally simple, requiring materials that are readily available, *i.e.*, a gas chromatograph, a temperature bath, a few septum-capped bottles, and gas-tight syringes.

INTRODUCTION

Headspace analysis has been in use for a number of years for identification of volatile organic compounds present in soil[1], foliage emissions[1,2], water[3,4], and foods[5]. The technique has also been used for the determination of gas–liquid partition coefficients[6-8], and has recently been reviewed[9]. Although the technique has potentially been available for the determination of thermodynamic properties of solutions since the inception of gas chromatography (GC), apparently very little use has been made of it for other than analytical purposes. A recent review of the application of headspace analysis to the characterization of solute–solvent interactions is of interest in this regard[10]. The method has been used in this laboratory for a number of years for analysis of the headspace vapors above military grade 2,4,6-trinitrotoluene (TNT)[11,12], but to the author's knowledge has not been used for the determination of vapor pressures.

The purpose of this paper is to describe the determination of the vapor pressure of TNT by the headspace method. Although the vapor pressure of this compound at room temperature is too low to be measured conveniently by the Knudsen technique[13], extrapolations of measurements made at higher temperatures[14-16] are in good agreement with the experimental results. Disagreement among several determi-

nations[14–17] of the vapor pressure of solid TNT may be due to the difficulty in obtaining a sample of the required purity. This problem is discussed in detail elsewhere[12]. A major advantage of the method reported here is that scrupulous purity is not necessarily required since the more volatile impurities, which interfere when weight loss is measured, are separated chromatographically prior to vapor pressure determination. Chromatographic analysis also permits identification and estimation of solid phase impurities and allows inferences to be made about the physical characteristics of the solid through application of Raoult's and Henry's laws[12].

EXPERIMENTAL

Materials and instrumentation

Samples were prepared for analysis by placing 2 g of substance in a 125-ml vial with a silicone rubber septum cap ("Hypovial", Pierce Rockford, Ill., U.S.A.). The vial was then placed in a thermostatted, well-stirred, water-bath (Forma Scientific, Marietta, Ohio, U.S.A.) by submerging the flask up to the neck. Temperature regulation was better than $\pm$ 0.5 °C. The experimental temperature was determined using three mercury thermometers which agreed to better than $\pm$ 0.5 °C. After equilibration for 2–4 weeks, gas samples were withdrawn using gas-tight syringes with fixed needles of 304 stainless steel (0.041 mm I.D.) and PTFE-tipped plungers (Hamilton, Reno, Nev., U.S.A.). Headspace GC was performed using a Perkin-Elmer Model 900 gas chromatograph equipped with a tritium foil electron capture detector (ECD). Chromatographic conditions were as follows:

Column, 1.8 m stainless steel (316)

· Packing, 10% Dexsil 300 GC on 100–120 mesh, Anakrom ABS (Analabs, North Haven, Conn., U.S.A.)

Carrier gas, specially purified nitrogen* at 50 ml/min

Temperatures, Injector, 250 °C; column, 190 °C; manifold, 200 °C; detector, 190 °C.

Detector, titanium tritide operated in the pulse mode at 50 V amplitude, 1-μsec pulse width, and 100-μsec pulse interval.

Under these conditions the major volatile impurities in TNT are separated from the 2,4,6-TNT peak. The TNT samples used for vapor pressure measurements were Eastman White Label (Lot No. 268) and a military-grade sample, recrystallized, and furnished through the courtesy of Mr. C. Ribaudo of Picatinny Arsenal (Dover, N.J., U.S.A.). Both were used without further purification. The detector response for TNT was determined by injection of a benzene solution of appropriate concentration. Typically, the working range for both vapor and solution samples was between 10^{-11} and 10^{-10} g, over which the detector response was found to be linear.

Method

Samples for vapor pressure determination were allowed to equilibrate for 2–4 weeks before withdrawal of headspace vapor for analysis. Prior experiments had shown that attainment of equilibrium was effected in this length of time[11]. It was

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* Purification consisted of successive traps containing ascarite, an oxygen scrubber ("Oxytrap", Analabs), and 80–100 mesh 5-A molecular sieve (Linde) maintained at −90 °C.

anticipated that adsorption of vapors on the glass barrel of the syringe might cause low recovery. Therefore it was thought that "pumping" the syringe a number of times might be necessary to effect equilibration with the barrel prior to injection of a sample for analysis. Initial studies using TNT which had been equilibrated at 23 °C (ref. 18) did, in fact, show that the observed concentration was dependent on the number of times the syringe was pumped, leading to erroneously high and unreproducible values. As described elsewhere[12], it was eventually found that the stainless-steel needle was such an efficient adsorber for this particular compound that complete recovery could be realized for up to several milliliters of vapor at this temperature. Once this had been discovered, it became an advantage analytically since any problems associated with adsorption on other parts of the syringe were eliminated, and the compound was easily desorbed from the needle by injection into the heated injector block during analysis. The technique adopted was to draw slowly an exact volume of vapor from the headspace, and to inject immediately into the gas chromatograph after wiping the outside of the needle with a tissue wetted lightly with acetone to remove any TNT which had been adsorbed during sampling. If less than 2.5 ml of vapor was taken for analysis, the syringe was filled to 2.5 ml with room air prior to injection in order to provide an adequate volume for flushing the needle during injection. When these precautions were followed good reproducibility was obtained. The difficulties associated with accurate sampling of headspace vapors of this type using gas-tight syringes are emphasized here and elsewhere[10] as a warning to others that there are potential problems associated with this method of sampling. These experimental factors must be investigated thoroughly for the particular compound to be investigated before vapor pressure determinations by headspace analysis are undertaken. In this case the problems were not insurmountable, perhaps due to the fortuituous capacity of the syringe needle as a vapor collector. In other cases more refined sampling techniques may be needed[10].

The concentration of TNT in the headspace vapor was determined by manual triangulation of the peak giving peak area/volume and dividing by the detector response factor (peak area/mass) as determined by injection of known quantities of TNT dissolved in benzene. Incidentally, when the electron capture cell contained a new source, the molar response for TNT (as measured in Ampere-sec or Coulombs) approached or exceeded the theoretical response of one electron per molecule (1 Faraday or 96.500 Coulombs per mole). Such "hypercoulometric" responses have recently been reported in this journal for this and other compounds in a d.c. ECD[19]. These authors indicated that lower (but still hypercoulometric) responses were obtained in the pulsed mode of operation, which is in agreement with experience in this laboratory.

RESULTS AND DISCUSSION

The concentration of TNT in equilibrium headspace vapor was determined experimentally in the range of 12–40 °C. Vapor pressure was calculated using the ideal gas law, $pV = nRT$, solving for p and expressing n as m/M, where m is the mass of TNT in g as determined by gas chromatography and M is the molecular weight of TNT in g/mole. V is the experimentally measured volume of vapor injected, T is the absolute temperature in °K, and R the gas constant. For computation of p in torr,

TABLE I

VAPOR PRESSURE OF TNT

T (°C)	No. of determinations	p (torr $\times 10^6$)	
		Mean	S.D.
12.0	9	0.27	0.09
20.0	16	1.10	0.22
21.5	14	1.72	0.42
25.5	4	3.98	0.19
30.0	13	8.82	0.29
40.0	13	42.4	3.10

R is most conveniently expressed as 62.36 liter-torr/mole °K. The experimental data are summarized in Table I.

The fundamental expression relating the vapor pressure of a solid to temperature is the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_g - V_s)}$$

where the volume of TNT in the gas phase is V_g, and in the solid phase V_s. The heat of sublimation (ΔH) is given by[20]

$$\Delta H = \int_0^P V_s \, dP + \int_0^T C_P \, dT$$

However, since the volume of solid is not appreciably affected by small (*i.e.*, < 1 atm) changes in external pressure[21] (P); only the change in heat capacity (at constant pressure) (C_P), with temperature need be considered. The temperature dependence of the heat capacity is generally recognized; therefore, ΔH will be treated as constant over only very short temperature ranges ($\sim$20 °K).

If it is further assumed that V_g is given by the ideal gas law —a good assumption since p is low at these temperatures— then the Clapeyron equation can be integrated to give

$$\ln p = -\frac{\Delta H}{RT} + B$$

in which B is a constant. Thus, if the assumptions are reasonable, a plot of $\ln p$ vs. $1/T$ should give a straight line of slope $-\Delta H/R$. The data of Table I are plotted in Fig. 1 along with data from the literature[14,15]. Visual inspection does show that the data of Table I are well represented by a straight line, and that a smooth curve can be constructed between literature values obtained at higher temperature and these data. The slight curvature in the line is an indication that a more complicated dependence of ΔH on T should be assumed in order to represent the vapor pressure of the solid up to its melting point. If it is more reasonably assumed that the difference in heat
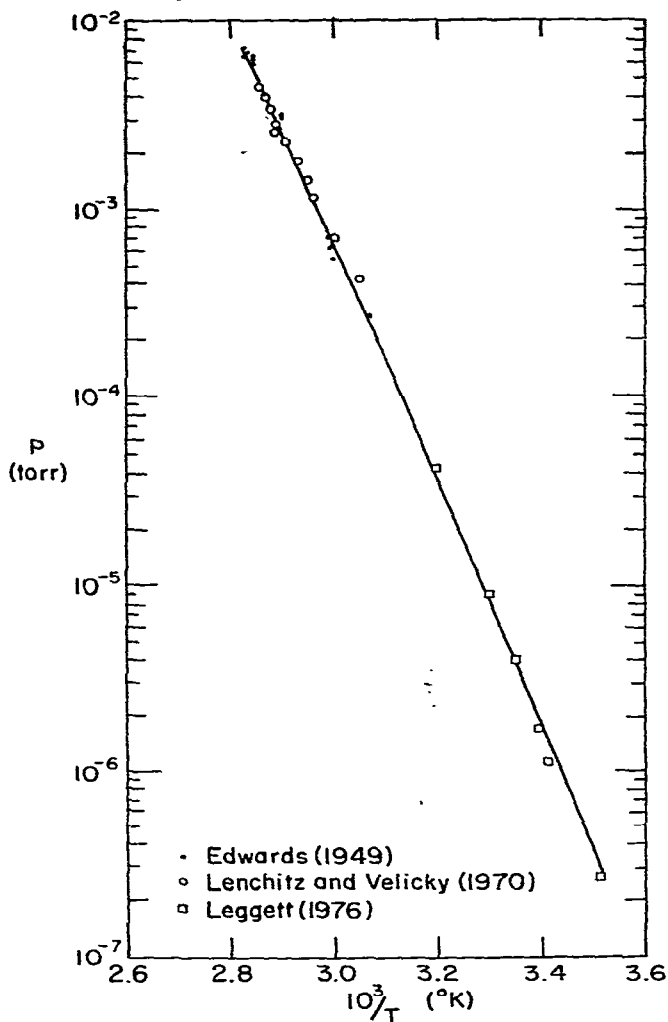
Fig. 1. Vapor pressure of 2,4,6-trinitrotoluene.

capacities between the solid and vapor is constant over the temperature range, then the Clapeyron equation integrates to $\ln p = -\Delta H/RT + B \ln T + C$[22,23].

For the purpose of this discussion, two, three, and four constant equations were fitted to the data, and the empirical constants for best fit obtained using a computer. The equations used were

$$\log p = A \left(\frac{1}{T}\right) + B \tag{1}$$

$$\log p = A \left(\frac{1}{T}\right) + B \log T + C \tag{2}$$

$$\log p = A \left(\frac{1}{T}\right) + B \log T + CT + D \tag{3}$$

TABLE II

MEASURED-*vs.* COMPUTED VAPOR PRESSURE VALUES (torr $\times 10^6$)

T ($°C$)	Measured*	Leggett**	Lenchitz and Velicky***	Edwards[§]	Wood[§§]	Coates et al.[§§§]
12	0.27	0.252	0.252	0.286	0.275	0.293
20	1.10	1.28	1.31	1.30	1.46	1.27
21.5	1.72	1 72	1.80	1.71	1.97	1.66
25.5	3.98	3.75	3.75	3.48	4.24	3.32
30	8.82	8.61	8.42	7.52	9.62	7.06
40	42.4	—	44.9	37.5	50.2	34.6

* Experimental values.
** $\log p = -7371.46 \, (1/T) + 19.2533$ (this work).
*** $\log p = -12521.73 \, (1/T) - 0.174972 \log T - 0.059896T + 54.82218$ (ref. 15).
[§] $\log p = -8328.404 \, (1/T) + 6.60587 \log T - 0.027236T + 14.21213$ (ref. 14).
[§§] $\log p = -12261.28 \, (1/T) + 5.910518 \log T - 0.0647905T + 40.40298$ (ref. 16).
[§§§] $\log p = -8389.86 \, (1/T) - 13.7567 \log T + 56.6639$ (ref. 22).

Using the data presented in Table I above, equally good fits were obtained using either eqn. 1 or 3, but not 2. Combining these data with each of the other three sets of data for solid TNT[14–16] gives a better fit with eqn. 3 than with eqn. 1, as expected. Highly acceptable fits ($r > 0.999$) are given in combination with the data of Edwards[14] or Lenchitz and Velicky[15]. The data of Wood[16] appear high, possibly due to sample purification problems, as discussed earlier. The experimental data determined by the headspace technique and predicted values using these equations are presented in Table II along with a published extrapolation of Edwards' data[22]. The best agreement with experimental data is given by the equation for the data presented here and those of Lenchitz and Velicky[15]. It is, therefore, the preferred equation of best fit for solid TNT over the entire range up to its melting point (81 °C). A good fit from 12–30 °C is given by the two-constant fit to the data of Table I, which may be preferred for simplicity. The heat of sublimation, over this range calculated from the slope constant, is 33.73 $\pm$ 0.05 kcal/mole (probability = 0.90).

To evaluate the effect of impurities on the measured vapor pressure, several samples of unpurified military production grade TNT were analyzed by the head-space method. These samples typically contain about 1 % of organic impurities other than 2,4,6-TNT, mainly other di- and tri-nitrotoluene isomers[12]. As shown in Table III, the vapor pressure measurement was relatively unaffected by this level of impurities.

TABLE III

EFFECT OF IMPURITIES ON VAPOR PRESSURE MEASUREMENTS

T ($°C$)	Experimental*	Predicted
12.0	0.27	0.252
20.0	1.19	1.28
21.5	1.51	1.72
23.0	2.28	2.30

* Average of eight determinations.

This is a major advantage of the headspace technique, as it is not always possible to purify compounds sufficiently for accurate determination by the effusion method. For example, the unpurified TNT samples contained about 0.1 mole %, 2,4-dinitrotoluene, which at equilibrium (20 °C) was present at a partial pressure of 2×10^{-5} torr above these samples, or 20 times higher than the vapor pressure of TNT at that temperature. Even recrystallized TNT was found to contain sufficient 2,4-dinitrotoluene to necessitate its separation prior to analysis (ref. 18). The other major advantage of this method is that it is sufficiently sensitive ($<10^{-7}$ torr) to permit determinations of very low pressures, for which ideality is more apt to be attained.

In summary, the vapor pressure of TNT determined by GC headspace analysis compared favorably with literature data obtained using the Knudsen effusion method. Although the method remains to be verified with other compounds, it is expected to be of general applicability and is recommended as an alternative approach for determining vapor pressure, which will be particularly useful when working with compounds of low volatility. Also, the criteria for purity do not have to be as stringent as when measuring weight loss. The sensitivity and resolution of GC should make this method particularly attractive for obtaining vapor pressure data at ambient temperatures, thus avoiding the hazards of extrapolation, and when working with compounds difficult to purify.

ACKNOWLEDGEMENTS

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