544 J. Chem. Eng. Data 2004, 49, 544−546

Sublimation Pressure and Vapor Molecular Weight of Pentaerythritol Tetranitrate

Kai H. Lau, Donald L. Hildenbrand,* Steven Crouch-Baker, and Angel Sanjurjo

SRI International, Menlo Park, California 94025

The sublimation pressure of crystalline pentaerythritol tetranitrate has been determined over the temperature range (356 to 382) K by the torsion−effusion method. From simultaneous mass-loss determinations, the molecular weight of effusing vapor was found to be in accord with that of monomeric $C(CH_2ONO_2)_4$. Effusing vapor was also examined by mass spectrometry, extending the temperature−pressure range down to 302 K. The temperature dependence of pressure, determined by both torsion and mass-spectrometric methods, yielded enthalpies of sublimation in close agreement at (157.4 ± 3.2) $kJ \cdot mol^{-1}$. Earlier pressure measurements in the literature are lower by nearly a factor of 3, and the corresponding second-law sublimation enthalpy is also significantly lower.

Introduction

Pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$ or PETN, is a commonly used high explosive. However, the sublimation pressure of PETN is one of the important physical properties that has not yet been accurately determined, despite the potential value in understanding certain behavioral characteristics associated with safe handling procedures. Edwards[1] initially measured the sublimation pressure of PETN by the Knudsen mass-loss method in the temperature range (370 to 412) K, below the melting point of 415 K. Later, Cundall et al.[2] reported sublimation pressures also measured by the Knudsen method in the range (328 to 405) K but with a presumably more sensitive mass-detection technique. Cundall et al.[2] report their results in equation form only and, in reference to the work of Edwards,[1] state that "agreement between these data and the present work is excellent." However, use of the reported[2] constants in the pressure equation for PETN yields sublimation pressures that are lower than those of Edwards[1] by a factor of nearly 10^4. There is clearly something wrong with the reported constants in the sublimation pressure equation of Cundall et al.,[2] and without access to the actual measured pressures, there is no reliable way to evaluate their results. We are not aware of any other published research on the vapor pressure of this material. This makes it all the more important to have additional measurements on PETN. We report here new sublimation pressure determinations made by means of the torsion−effusion method, with simultaneous mass-loss measurements. The torsion results give absolute total pressures, while the mass-loss data yield vapor molecular weights that give information about vapor composition. In addition, the mass spectrum of PETN equilibrium vapor was examined to obtain further information about vapor composition and the temperature dependence of sublimation pressure.

Experimental Methods

Apparatus and Procedures. The torsion vapor pressure system is basically an effusion manometer, in which a two-chamber cell with offset orifices in opposite positions on opposite faces is suspended from a small-diameter filament attached to the arm of a microbalance, all within an evacuated enclosure. Effusion of vapor induces a recoil force and consequent angular rotation of the cell. This is a purely mechanical device that yields absolute total pressure in terms of the torsion constant of the filament, the observed angular deflection, and the geometrical constants of the cell. Since effusion pressure evaluated from mass-loss alone requires knowledge of vapor molecular weight, M, then determination of torque angle and mass-loss together allows one to evaluate M directly. Effusion measurements have an upper pressure limit of about 10 Pa because of mean free path restrictions for maintaining free molecular flow through the exit orifice. All of the measurements reported here were made with two Pt−Rh cells having nominal orifice diameters of 0.06 (P2) and 0.11 (P1) cm. Temperatures were measured with a Pt, Pt−Rh thermocouple of accurately established calibration, equivalent to an accuracy of 0.1 K. Frequent checks with laboratory vapor pressure standards such as Ag, Sn, and KCl have shown that both absolute pressures and vapor molecular weights are accurate to within 5% and that second-law slope enthalpies can regularly be measured with an accuracy of (2.1 to 4.2) $kJ \cdot mol^{-1}$ or better. Stated uncertainties in the Results section are absolute uncertainties based on comparisons with standards, while uncertainties in coefficients of vapor pressure equations in the Tables are statistical values from least-squares fitting. The torsion−effusion system and microbalance arrangement for simultaneous measurement of effusion recoil force and sample mass loss has been described in the literature.[3,4] Mass-spectrometric studies of PETN vapor were made with the magnetic sector instrument used in earlier work.[5]

Chemicals. The crystalline PETN sample was obtained from Accurate Energetic Systems, McEwen, TN. Although no statement of sample purity was provided by the supplier, the vapor mass spectrum agreed closely with a published spectrum,[6] showing only the two major peaks identified with PETN. Several minor peaks, observed initially, disappeared after about 30 min of outgassing at

---

* To whom correspondence may be addressed. E-mail: donald.hildenbrand@sri.com. Fax: 650-859-2111.

10.1021/je0302203 CCC: $27.50

Table 1. Sublimation Pressure and Vapor Molecular Weight of PETN(s) by Use of the Torsion−Effusion Method[a]

T/K	P/Pa	M/g·mol^{-1}
363.2	8.52×10^{-2}	348
374.9	4.46×10^{-1}	339
373.0	3.42×10^{-1}	351
361.9	7.50×10^{-2}	362
356.9	3.53×10^{-2}	
369.2	2.08×10^{-1}	336
376.6	5.76×10^{-1}	341
379.0	7.62×10^{-1}	335
380.5	9.44×10^{-1}	326
380.8	9.58×10^{-1}	330
382.0	1.15	330
376.2	4.86×10^{-1}	341
361.1	6.42×10^{-2}	333
356.1	3.01×10^{-2}	
	Average =	339

[a] Pt−Rh cell P2, 0.06-cm diameter orifice; $\log(P/\mathrm{Pa}) = (21.511 \pm 0.13) - (8197 \pm 48)\mathrm{K}/T$. $\Delta H°_{371} = (156.9 \pm 0.8)$ kJ/mol.

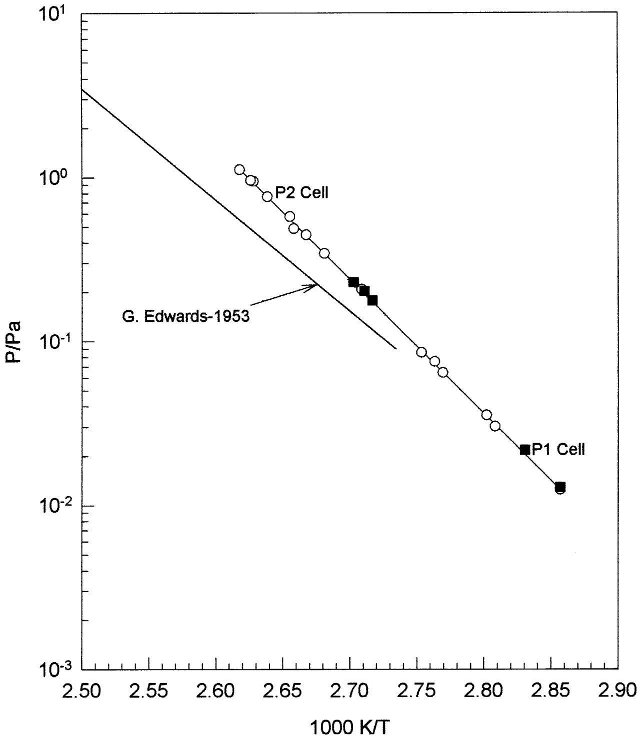

Figure 1. Total vapor pressure of PETN measured with two platinum−rhodium effusion cells for the sublimation process PETN(s) = PETN(g).

320 K in the spectrometer vacuum system. In addition, the torsion sublimation pressures were highly stable and reproducible throughout. It is believed that the clean vapor mass spectrum and the steady sublimation behavior indicate the sample to be of acceptable purity, estimated to be 99.9% or better.

Results

In Table 1 and Figure 1 are shown the sublimation pressures measured over the range (350 to 382) K with the two torsion cells of different orifice size. Measurements were made in the random order shown and were found to be highly stable and reproducible. Although the orifice areas of the two cells differ by about a factor of 3, the pressures agree to within a few percent, indicating them to be equilibrium saturation values, free of any kinetic effects.

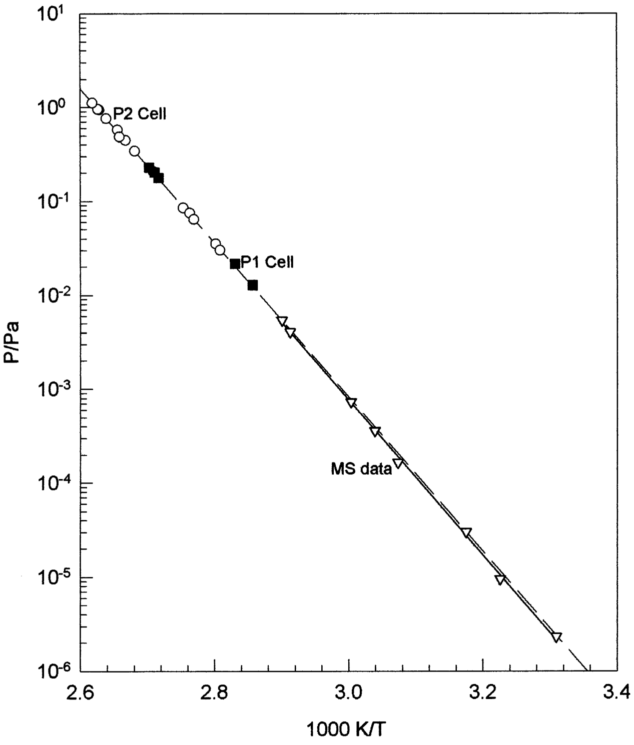

Figure 2. Total vapor pressure of PETN measured with two platinum−rhodium effusion cells and with a mass spectrometer for the sublimation process PETN(s) = PETN(g).

Furthermore, the average vapor molecular weights of (339 and 328) g·mol^{-1} are within 4−7% of the $C(CH_2ONO_2)_4$ monomer value of 316.1, showing that the simple monomeric reaction

$$C(CH_2ONO_2)_4(s) = C(CH_2ONO_2)_4(g) \qquad (1)$$

characterizes the PETN sublimation process. The slightly higher experimental molecular weights are within the demonstrated accuracy of the technique, and are not indicative of a small amount of polymeric vapor species. Further, the high-sensitivity mass-spectrometric analysis shows no evidence for higher polymers of $C(CH_2ONO_2)_4$. Table 1 also gives the least-squares derived coefficients in the sublimation pressure equation

$$\log(P/\mathrm{Pa}) = A - (B/T) \qquad (2)$$

derived from the more extensive pressure measurements with cell P2, leading to the second-law sublimation enthalpy of (156.9 ± 3.2) kJ·mol^{-1} at the average temperature of 371 K. The five pressure points measured with cell P1 over a narrow temperature range were obtained only to demonstrate the absence of orifice-size kinetic effects and are not sufficient for accurate second-law analysis.

Investigation of the mass spectrum of effusing vapor from a Pt cell at about 350 K showed only the two peaks at (46 and 76) amu, identified as NO_2^+ and $CH_2ONO_2^+$, respectively, formed by electron-impact fragmentation of $C(CH_2ONO_2)_4$, in accord with the reported[6] mass spectrum. The parent ion is unstable and yields the two fragment ions with appearance energies of 12.1 eV (NO_2^+) and 12.6 eV ($CH_2ONO_2^+$), both ±0.5 eV. Eight measurements of the NO_2^+ intensity at 30-eV ionizing energy over the range (302 to 345) K, shown in Figure 2 yielded a second-law sublimation enthalpy of (158.2 ± 3.3) kJ·mol^{-1}, in good agreement with the value obtained from the torsion pressure determinations.

Table 2. Sublimation Pressure and Vapor Molecular Weight of PETN(s) by Use of the Torsion−Effusion Method[a]

T/K	P/Pa	M/g·mol^{-1}
368.1	1.77×10^{-1}	325
368.9	2.04×10^{-1}	322
370.0	2.30×10^{-1}	324
350.1	1.28×10^{-2}	
353.3	2.17×10^{-2}	340

[a] Pt−Rh cell P1, 0.10-cm diameter orifice.

Discussion

As seen in Figure 1, the torsion−effusion sublimation pressures of PETN reported here are higher by a factor of 3 than the results of Edwards,[1] obtained by the effusion mass-loss technique. It is worth noting that complex materials do not necessarily vaporize to the single monomeric gaseous molecules; saturated vapors of some metal carbonyls have been found to be largely dimeric or trimeric.[7,8] Evaluation of equilibrium vapor pressure from effusion mass-loss measurements alone requires some knowledge or assumption about the nature of the vapor species. Of course Edwards[1] had no direct evidence for the monomeric character of the vapor, but our vapor molecular weight determinations confirm this and permit his reported pressures to be compared with our absolute torsion pressure values. Because checks with lab standards have shown our torsion pressures to be accurate within 5%, we believe that our values are preferable to those of Edwards,[1] who gave no accuracy estimate.

The torsion pressure and mass-spectrometric second-law enthalpies of sublimation for reaction 1, (156.9 ± 3.2) kJ·mol^{-1} at an average temperature of 371 K, and (158.2 ± 3.2) kJ·mol^{-1} at 325 K, are in close agreement, indicating that ΔC_p for the process is relatively small and ΔH(sub) is nearly constant over the range (302 to 382) K. We adopt the value of $\Delta H°_{298}$(sub) = (157.4 ± 3.2) kJ·mol^{-1}, which is an average of the torsion-pressure and mass-spectrometric values. Edwards[1] reported a ΔH (sub) value of (151.9 ± 2.1) kJ·mol^{-1} at an average temperature of 393 K, which would be in reasonable accord with our value. However, a least-squares treatment of his published results[1] actually yields a ΔH(sub) value of 141.8 kJ·mol^{-1}, substantially lower than our value of 157.4 kJ·mol^{-1}. If the NO_2^+ intensity is normalized to the extrapolated torsion pressure at 344.8 K, the intensities at lower temperatures can be converted to absolute pressures, extending these values to the full range (302 to 382) K.; these pressures derived from the NO_2^+ intensities are listed in Table 3. The equation

Table 3. Sublimation Pressure of PETN(s) from Mass-Spectrometric NO_2^+ Intensities[a]

T/K	P/Pa	T/K	P/Pa
329.0	$3.59 \times 10-4$	343.3	$4.08 \times 10-3$
315.0	$3.02 \times 10-5$	325.4	$1.64 \times 10-4$
302.2	$2.31 \times 10-6$	310.0	$9.50 \times 10-6$
333.0	$7.31 \times 10-4$	344.8	$5.41 \times 10-3$

[a] $\log(P/\mathrm{Pa}) = (21.674 \pm 0.27) - (8263 \pm 87)\ \mathrm{K/T}$; $\Delta H°_{325} = (158.2 \pm 1.7)$ kJ/mol.

$$\log(P/\mathrm{Pa}) = 21.511 - (8197/T) \quad (3)$$

derived from the torsion pressures with cell P2 represents the pressure data well over this range, as seen in Figure 2. Extrapolation of the torsion pressures alone yields a calculated sublimation pressure of 2.4×10^{-6} Pa at 302.2 K, compared to the value 2.3×10^{-6} Pa obtained from the normalized ion intensities. At normal room temperature, 298 K (25 °C), eq 3 indicates the vapor pressure of PETN to be 1×10^{-6} Pa or 8×10^{-9} mm Hg.

Literature Cited

(1) Edwards, G. The Vapour Pressure of Cyclo-Trimethylenetrinitramine (Cyclonite) and Pentaerythritoltetranitrate. *Trans. Faraday Soc.* **1953**, *49*, 152−154.
(2) Cundall, R. B.; Palmer, T. F.; Wood, C.E. C. Vapour Pressure Measurements on Some Organic High Explosives. *J. Chem. Soc., Faraday Trans. 1* **1978**, 74, 1339−1345.
(3) Lau, K. H.; Cubicciotti, D.; Hildenbrand, D. L. Effusion Studies of the Decomposition of Magnesium and Calcium Sulfates. *J. Chem. Phys.* **1977**, *66*, 4532−4539.
(4) Colominas, C.; Lau, K. H.; Hildenbrand, D. L.; Crouch-Baker, S.; Sanjurjo, A. Vapor Pressures of the Copper and Yttrium β-Diketonate MOCVD Precursors. *J. Chem. Eng. Data* **2001**, *46*, 446−450.
(5) Lau, K. H.; Hildenbrand, D. L. Thermochemistry of the Gaseous Uranium Bromides UBr through UBr_5. *J. Chem. Phys.* **1987**, *86*, 2949−2954.
(6) Stein, S. E. "Mass Spectra" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69. Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, 2003 (http://webbook.nist.gov).
(7) Chandra, D.; Garner, M. L.; Lau, K. H. Vapor Pressure of Osmium, Rhodium, and Ruthenium Carbonyls. *J. Phase Equilib.* **1999**, *20*, 565−572.
(8) Garner, M. L.; Chandra, D.; Lau, K. H. Low-Temperature Vapor Pressures of W-, Cr-, and Co−Carbonyls. *J. Phase Equilib.* **1995**, *16*, 24−29.

Received for review August 20, 2003. Accepted March 5, 2004.

JE0302203