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Vapor Pressure of Solid Polybrominated Diphenyl Ethers Determined via Knudsen Effusion Method

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Abstract

Polybrominated diphenyl ethers (PBDEs) are flame retardants used in a variety of consumer products. The solid vapor pressures of BDE15 and BDE209 were determined by use of the Knudsen effusion method, and the values measured extrapolated to 298.15 K are 3.12×10^{-3} and 9.02×10^{-13} Pa, respectively. The enthalpies of sublimation for these compounds have also been estimated by using the Clausius-Clapeyron equation and are 102.0 ± 3.5 and 157.1 ± 3.5 kJ/mol, respectively. Additionally, the melting points and enthalpies of fusion were measured by differential scanning calorimetry.

Keywords

PBDE; Solid vapor pressure; Knudsen effusion; Enthalpy of sublimation; Enthalpy of fusion

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are flame retardants that have been used for more than three decades in electronic equipment and building materials such as circuit boards, capacitors, and textiles [1]. Owing to their persistence and probable carcinogenic human health effects, PBDEs have received considerable attention from scientists [2]. The accumulation of PBDEs in sediment and biota of aquatic environments is regarded as a serious environmental problem around the world [3–5]. Polybrominated diphenyl ethers differ from most other persistent organic pollutants in two important ways. First, the source of exposure is in indoor dust rather than food as for other persistent pollutants. For this reason, researchers have begun to call PBDEs “indoor persistent organic pollutants”. second, their distribution is uneven in humans [6]. In 2004, Europe banned the use of two formulations of PBDE, pentaBDE and octaBDE, and the same year they were withdrawn from the North American market. A third compound, decaBDE, was banned on 1 April 2008 by the European Court of Justice. For the U.S., Maine has banned the use of decaBDE (the only PBDE still on the market in North America) in mattresses and residential upholstered furniture produced and sold in that state [7]. Concerns have also arisen about the PBDEs due to their appreciable concentration increase in remote regions and in mothers’ milk [8, 9]. The structure of PBDEs is similar to other classes of halogenated organic compounds, such as polychlorinated biphenyls and dioxin, which suggests a potential dioxin-like toxicity.

PBDEs include 209 congeners with similar structures and could be divided into 10 groups (mono-to decabromobiphenyl ethers) depending on the number and the position of bromine atoms on the two aromatic rings. The PBDEs in the first group, i.e. monobromobiphenyl

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ethers are mostly in a liquid state at room temperature, whereas PBDEs in other groups are mostly in the solid state.

The knowledge of physicochemical properties of PBDEs is essential in understanding the distribution of PBDEs in the environment. This knowledge is also important to those involved with manufacturing or waste treatment processes of products containing PBDEs. However, only limited data are generally available for PBDEs [10–17], especially vapor pressure data. Vapor pressure determines the tendency of a chemical to transfer to and from gaseous environmental phases and these data are critical for prediction of both the equilibrium distribution and the rate of transport to and from sinks and sources [18]. The hypothetical subcooled liquid vapor pressures for 31 PBDEs have earlier been measured using the GC-retention time method [14, 15, 17]. However, no actual solid state vapor pressure data have been reported for PBDEs, and this is the phase in which most of these compounds exist in the pure state at ambient condition.

In the present study, the solid state vapor pressures of two pure PBDEs, i.e. 4,4-dibromodiphenyl ether (BDE15 in the second group), and decabromodiphenyl ether (BDE209 in the tenth group) were measured using the Knudsen effusion method. The enthalpy of fusion and melting point of these two PBDEs were also determined by differential scanning calorimetry. The solid vapor pressure of BDE15 is also compared with earlier reported GC-retention data, adjusting from the subcooled liquid to actual solid state.

MATERIAL AND METHODS

Chemicals

4,4-dibromodiphenyl ether (BDE15) (CAS Reg. No. 2050-47-7, with mass fraction purity > 0.97 and $M = 328.0$ g/mol), and decabromodiphenyl ether (BDE209) (CAS Reg. No. 1163-19-5, with mass fraction purity > 0.98 and $M = 959.2$ g/mol) were purchased from TCI America. They were used without further purification, except as noted below.

Melting temperature and enthalpy of fusion

Temperatures and enthalpies of fusion were measured using a TA Instruments 2910 differential scanning calorimeter (DSC). A 3 to 5 mg sample was placed into a hermetically sealed DSC pan and was scanned at 10 K/min. The uncertainty in reported enthalpies of fusion is about ± 5 J/g.

Vapor pressure

The Knudsen effusion technique was used to measure vapor pressures. This is an indirect measurement technique based on the molecular effusion of a vapor through an orifice into a high vacuum and it is generally used to measure the vapor pressure of low volatility substances. The vapor pressure of a substance can be obtained from effusion data using

$$P = \frac{\omega}{tAW} \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where ω is the weight loss during the effusion time interval t , A is the orifice area, R is the universal gas constant, T is the sample temperature, M is the molecular mass of the effusing species, and W is the Clausing correction factor. W ranges from 0 to 1 and quantifies the probability of molecular escape from the effusion cell [19]. W is calculated from the empirical formula

$$W = \frac{1}{1 + (3l/8r)} \quad (2)$$

where l is the orifice effusion length and r is the orifice radius. In these experiments, W calculated by using equation 2 was always very close to 0.97. These values have also been experimentally verified, using calibration compounds of known vapor pressure [20].

Samples were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice 0.61 ± 0.02 mm in diameter, and then placed on one arm of a continuously recording microbalance (Cahn 2000) with a sensitivity of 0.5 μ g and a 100-mg capacity. The entire assembly was pumped to a high vacuum with the pressure inside of the chamber reduced to 10^{-4} Pa. The measurements were made under isothermal conditions by using a type K thermocouple located directly right above the effusion cell, accurate to ± 0.1 K, calibrated with a National Institute of Standards and Technology traceable thermometer. The temperature and mass are recorded continuously in order to obtain an average mass loss rates over an extended period. Therefore, the relative instrument uncertainty within the experimental temperature range is about $\epsilon_P = \delta P/P = 0.05$. Before commencing data collection, over 5 % of the compound in the cell was sublimed to ensure removal of any volatile impurities, and this has also been observed by mass spectrometry to be sufficient to obtain pure compound results even when starting with commercial purity samples [21]. Additionally, the data collection was stopped before over 95 % of the sample in the cell sublimated in case there were any nonvolatile impurities present.

To verify the reliability of the experimental technique, the reference compound anthracene was periodically employed to test the performance of the Knudsen effusion apparatus and the results were in good agreement with literature values [20, 22–24]. More details of this technique can be found in [19, 20, 25, 26].

RESULTS AND DISCUSSION

The measured melting points and enthalpies of fusion ($\Delta_{\text{fus}}H$) for BDE15 and BDE 209 are given in Table 1. The melting temperatures are generally in good agreement with literature data, 330.15 K to 333.5 K for BDE15, and 575.6 K to 578.2 K for BDE209 [13, 27]. No enthalpy of fusion data could be found in the literature for these two PBDEs. The enthalpy of fusion data are needed to correct the subcooled state vapor pressures to real solid state vapor pressures (see below).

Table 2 presents the raw data obtained in the present experiment using the Knudsen effusion method. These data were used to calculate the enthalpy ($\Delta_{\text{sub}}H$) and entropy ($\Delta_{\text{sub}}S$) of sublimation, and vapor pressure at 298.15 K using the Clausius-Clapeyron equation, integrated assuming a constant enthalpy of sublimation,

$$\ln \frac{P}{P_0} = - \frac{\Delta_{\text{sub}}H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (3)$$

where R is the universal gas constant, T is the absolute temperature of the sample ($T < T_m$), and P_0 and T_0 refer to a reference state.

Table 3 details the quantities calculated from the data in Table 2. The enthalpy of sublimation of BDE209 is about 55 kJ/mol higher than that of BDE15 and the difference in entropy of sublimation of these compounds at 298.15 K is about 185 J/mol/K. Moreover, the vapor pressure at 298.15 K for BDE15 is about 9 to 10 orders of magnitude higher than that

of BDE209, which shows the strong decrease of vapor pressure with the increasing number of bromine atoms on the aromatic rings of PBDEs.

The vapor pressure of BDE15 is shown in Figure 1. It should be noted that the highest temperature point from the present study was attained for a liquid sample at 333.5 K, about 2 degrees higher than its melting temperature, 331.9 K. This point is seen to approach the estimates of subcooled liquid vapor pressure from GC-retention time studies, $\log(P_L/\text{Pa}) = -4074/(T/\text{K}) + 11.65$ [15], and $\log(P_L/\text{Pa}) = -3528/(T/\text{K}) + 10.08$ [17], which report virtual subcooled liquid state vapor pressure.

The subcooled liquid vapor pressure (P_L) of BDE15 was converted to solid vapor pressure (P_S) at any given temperature by

$$\ln P_L/P_S = \Delta_{\text{fus}}S(T_m - T)/(RT) \quad (4)$$

where T_m is the melting temperature and $\Delta_{\text{fus}}S$ is the entropy of fusion, and where $\Delta_{\text{fus}}S = \Delta_{\text{fus}}H/T_m$.

The enthalpies of vaporization for subcooled BDE15 liquid estimated by Wong et al. [15] and Tittlemier et al. [17] were 78.0 and 67.6 kJ/mol, respectively. After the adjustment by equation 4, enthalpies of sublimation estimated by equation 3 are 95.4 and 85.9 kJ/mol, respectively, which are still lower than the measured solid enthalpy of sublimation from the present study, 102.0 kJ/mol. Additionally, the estimated solid vapor pressure calculated from the subcooled vapor pressure data of Wong et al. is still 15% to 50% higher than the data obtained from the present study, while the difference from the values based on the data of Tittlemier et al. are even greater. It should be emphasized that correction from the virtual subcooled liquid state is essential, as near ambient temperatures vapor pressures predicted based on that state, 1.73×10^{-2} Pa [17], can be almost an order of magnitude too high in comparison to actual solid state values, 3.12×10^{-3} Pa.

Figure 2 shows the vapor pressures of BDE209 compared to those of BDE15. No published vapor pressure data have been found for the former compound. The vapor pressures of BDE15 are about 9 orders of magnitude higher than those of BDE209. With an increase of the number of bromine substitutions, the vapor pressure obviously drops sharply and the enthalpies of fusion and sublimation both increase significantly. Extrapolating to near ambient temperatures, the vapor pressures of BDE209 is negligible ($< 10^{-12}$ Pa).

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Figure 1.

Vapor pressures of 4,4-dibromodiphenyl ether (BDE15) obtained by using the Knudsen effusion method compared to available literature values obtained by using gas chromatography (GC)-retention time method. Published virtual subcooled liquid state data are shown as " P_L " values, and values corrected to actual solid state are shown as " P_s " values. Data measured in the present study on actual solid state samples are shown as data points and associated regression line.

Figure 2. Sublimation vapor pressures of decabromodiphenyl ether (BDE209) and BDE15. Both sets of data were obtained by using the Knudsen effusion method on pure solid samples.

Table 1

Melting points and enthalpies of fusion of polybrominated diphenyl ethers (PBDEs) examined in the present study.

Compound	Melting point (K)	$\Delta_{\text{fus}}H$ (kJ/mol)	Molecular structure
BDE15	331.9	18.4
BDE209	580.4	38.7

Table 2

Summary of vapor pressure data obtained using the Knudsen effusion method.

<i>T</i> (K)	<i>P</i> (Pa)	<i>T</i> (K)	<i>P</i> (Pa)
BDE15		BDE209	
300.0	0.00403	444.0	0.00111
303.9	0.00723	449.1	0.00193
308.7	0.0127	454.1	0.00288
313.6	0.0238	459.2	0.00329
318.7	0.0358	464.1	0.00513
323.6	0.0871	469.3	0.00855
328.6	0.150	474.3	0.0141
333.5 (liquid)	0.236	479.4	0.0222
		484.6	0.0356
		489.7	0.0523
		494.8	0.0808
		499.8	0.125
		504.8	0.181

Table 3

Enthalpies of sublimation derived from data in table 2 using the Clausius-Clapeyron equation. Also shown are entropies of sublimation and vapor pressures extrapolated to $T = 298.15$ K

Compound	Temp range (K)	$\Delta_{\text{sub}}H$ (kJ/mol)	$\Delta_{\text{sub}}S$ (J/mol·K) (298.15K)	P (Pa) (298.15K)
BDE15	300 – 328	102.0 ± 3.5	342.1 ± 11.7	3.12×10^{-3}
BDE209	444 – 505	157.1 ± 3.5	526.9 ± 11.7	9.02×10^{-13}