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Vapor Pressure of Three Brominated Flame Retardants Determined via Knudsen Effusion Method

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Abstract

Brominated flame retardants (BFRs) have been used in a variety of consumer products in the past four decades. The vapor pressures for three widely used BFRs, that is, tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and octabromodiphenyl ethers (octaBDEs) mixtures, were determined using the Knudsen effusion method and compared to those of decabromodiphenyl ether (BDE209). The values measured extrapolated to 298.15 K are 8.47×10^{-9} , 7.47×10^{-10} , and 2.33×10^{-9} Pa, respectively. The enthalpies of sublimation for these BFRs were estimated using the Clausius-Clapeyron equation and are 143.6 ± 0.4 , 153.7 ± 3.1 , and 150.8 ± 3.2 kJ/mole, respectively. In addition, the enthalpies of fusion and melting temperatures for these BFRs were also measured in the present study.

Keywords

Brominated flame retardant; Solid vapor pressure; Knudsen effusion; Enthalpy of sublimation; Enthalpy of fusion

Introduction

Brominated flame retardants (BFRs) have been used for more than four decades in electronic equipment and building materials such as circuit boards, capacitors, and textiles to increase their flame resistance [1]. The addition of BFRs is one of the lowest cost ways to meet flammability regulatory requirements. The most intensively used BFRs are tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and three commercial mixtures of polybrominated diphenyl ethers (PBDEs), that is, decabromodiphenyl ether (BDE209), octabromodiphenyl ethers (octaBDEs), and pentabromodiphenyl ethers (pentaBDEs).

Recently, many environmental studies have focused on PBDEs, owing to their persistence and probable carcinogenic human health effects [2]. The accumulation of PBDEs in sediment and biota of aquatic environments is regarded as a serious environmental problem around the world [3–5]. European and North American countries banned the use of pentaBDEs and octaBDEs in 2004. Decabromodiphenyl ether, the mostly widely used in all markets, was banned on April 1, 2008 by the European Court of Justice. In the United States, Maine has banned the use of BDE209 (the only PBDE still on the market in North America) in mattresses and residential upholstered furniture produced and sold in that state [6].

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Hexabromocyclododecanes, as an alternative to BDE209, have been increasingly used in Europe and Asia in recent years, and studies have shown that the levels of α -HBCD, the most persistent of the HBCDs, are increasing in biota and humans [7, 8]. However, HBCDs are presently only banned in Norway [9]. Tetrabromobisphenol A, which represents half of the usage of BFRs globally, has been detected in various environmental media and biota, such as water, air, soil, and sediments [10]. Nevertheless, owing to its low potential for bioaccumulation [11], no restrictions have currently been placed on the production of TBBPA [9].

Vapor pressure data are important parameters for models that predict the fate and transport of such BFRs in the environment. However, few vapor pressure data have been reported for these BFRs. Because of their high molecular weight and their degradation at high temperatures [12–17]. Therefore, it is desirable to employ techniques that can measure relatively low vapor pressures to study this property of these BFRs. Beyond the vapor pressures themselves, these data offer insights into other thermodynamic properties of these materials, such as cohesive energy in the condensed phase (related to the sublimation enthalpy).

The gas chromatography-retention time method has been employed to measure the hypothetical subcooled liquid state vapor pressure of 31 PBDEs [14–16], but this method could not be used to measure the vapor pressures of octaBDEs and BDE209. Because of their strong affinity to the generally employed column. In addition, it should be noted that most BFRs are in a solid state, not a liquid state, at ambient temperature, so that the subcooled liquid state data need to be corrected to a real state, if they are to be used.

In the present study, the solid state vapor pressures of three BFRs, i.e. TBBPA, HBCD, and octaBDE, were measured using the Knudsen effusion method, which has been successfully used by our group to measure the vapor pressure of BDE209 [17]. The enthalpies of phase change and melting temperature range of these BFRs were also determined by using a differential scanning calorimetry and melting point apparatus. The solid vapor pressures of these BFRs were also compared with those of BDE209.

Material and methods

Materials

Tetrabromobisphenol-A (CAS Reg. No. 79-94-7, with mass fraction purity > 0.98 and $M = 543.9$ g/mol), and HBCD (CAS Reg. No. 3194-55-6, with mass fraction purity > 0.95 and $M = 641.7$ g/mol), were purchased from TCI America. A mixture of octaBDEs isomers, ($M = 801.4$ g/mol), was purchased from Aldrich. The octaBDE is therefore not a “pure” compound like others. Nonetheless, vapor pressure data were obtained on the mixture. All these compounds were used without further purification, except as noted below.

Melting temperature and enthalpy of fusion

Melting temperatures of the samples (see Table 1) were measured using a Mettler Toledo MP50 melting point system, which also records the videos of the melting process. A total of 1 mg to 2 mg of each sample was placed in a capillary and heated at 1 ± 0.1 K/min, and melting was determined visually. The enthalpies of fusion were measured using a TA instruments 2910 differential scanning calorimeter (DSC). A 2 mg to 4 mg sample was placed into a hermetically sealed DSC pan, and this was scanned in heating mode at a heating rate of 10 K/min. The uncertainty in the DSC measurement is about ± 5 J/g. More details of this technique can be found in previous publications [18,19].

Vapor pressure

The Knudsen effusion method was employed to determine the vapor pressure of these three BFRs. This method derives from Knudsen's 1909 Kinetic Theory of Gases and is an indirect measurement technique. It based on measuring the molecular leak rate through a small orifice from an effusion cell into a high vacuum chamber. This method is generally used to measure the vapor pressure of low volatility substances. The vapor pressure of a substance is 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 [20]. 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.

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 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 to obtain an average mass loss rate over an extended period. Therefore, the relative instrument uncertainty within the experimental temperature range is about $\varepsilon_P = \delta P/P = 0.05$.

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 confirmed 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 sublimed 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 [22–25]. More details of this technique can be found in Fu and Suuberg [17], Fu et al. [18], Fu and Suuberg [19], and Oja and Suuberg [20].

Results and Discussion

The melting point apparatus and DSC were used to study the phase change behaviors of these BFRs, and the results are given in Table 1. The melting temperatures of TBBPA and HBCD are generally in good agreement with values summarized in the SciFinder compound database (<https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf>), 452 K to 454 K and 447 K to 472 K, respectively. The octaBDE mixture starts to melt at 409.2 K,

which is its thaw temperature [26], and the mixture is all in a liquid state at 433.2 K. This indicates that the mixture has a wide melting range, over 20 K. The melting temperatures and enthalpies of fusion of these three BFRs are all lower than that of BDE209 (580.4 K and 38.7 kJ/mol, respectively). Bearing in mind the DSC measurement uncertainty of $\pm 5 \text{ J} \cdot \text{g}^{-1}$, the present measured values would have an inherent uncertainty of 2.7 to 4.0 kJ $\cdot$ mol $^{-1}$.

Table 2 presents the raw vapor pressure data of TBBPA and HBCD obtained in the present experiment using the Knudsen effusion method. The data for octaBDE mixture are not listed in the table, because this commercial mixture does not have purity and concentration information. The raw vapor pressure data were used to calculate the sublimation enthalpy ($\Delta_{\text{sub}}H$) 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 ($T < T_{\text{fus}}$), and P_0 and T_0 are values at a related reference condition. The integrated form of Clausius-Clapeyron equation can also be written as

$$\log P = \frac{B}{T} + A \quad (4)$$

where

$$B = - \frac{\Delta_{\text{sub}}H}{2.303R} \quad (5)$$

Table 3 lists the results of fitting the data with Equation 3 along with the statistical significance of these results. The enthalpy of sublimation value presented here is calculated from the slope of the Clausius-Clapeyron equation for the temperature range indicated in Table 2. The slope B and intercept A of Equation 4 are also listed in the table.

Octabromodiphenyl ethers vapor pressure

The slope and intercept obtained for the octaBDE mixture are also included in Table 3. The vapor pressure of a PBDE congener is strongly related to its bromine content, which means that the vapor pressures of all octaBDE congeners are expected to be similar, particularly in comparison with congeners with different bromine contents. Figure 1 illustrates the relationship between the subcooled liquid state vapor pressure of PBDE congeners at 298.15 K ($P_{\text{L},298.15\text{K}}$) and their bromine contents. The virtual subcooled liquid state vapor pressures of the PBDE congeners, except the octaBDEs and BDE209, were measured by Tittlemier et al., using gas chromatography-retention time methods [14]. The solid vapor pressures (P_{S}) of octaBDE and BDE209 [17] measured in this laboratory were converted to subcooled liquid vapor pressures (P_{L}) at any given temperature by

$$\ln P_{\text{L}}/P_{\text{S}} = \Delta_{\text{fus}}S(T_{\text{fus}} - T)/RT \quad (6)$$

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

The slope of the regression line (see Figure 1) indicates that a substitution of a bromine for a hydrogen atom will decrease $P_{L,298.15K}$ approximately ninefold, which is consistent with the slope of a similar regression performed by Tittlemier et al., -0.9618 [14].

Figure 2 provides the vapor pressure data of the octaBDE mixture in comparison to the values for 4,4'-dibromodiphenyl ether (BDE15) and BDE209, which were also determined earlier by using the Knudsen effusion method [17]. The enthalpy of sublimation of the octaBDE mixture is similar to, but about 7 kJ/mol lower than that of BDE209 (157.1 ± 3.5 kJ/mol), but about 48 kJ/mol higher than that of BDE15 (102.0 ± 3.5 kJ/mol [17]). The solid state vapor pressure of octaBDE mixture at 298.15 K is about 4 orders of magnitude higher than that of BDE209, whereas it is approximately 6 orders of magnitude lower than that of BDE15.

Thus, vapor pressures of the full suite of PBDE congeners are now available, at least in the hypothetical subcooled liquid state. There is an unresolved issue related to the correction of the values of vapor pressure and enthalpy of sublimation from the subcooled liquid state to the ambient temperature solid state of practical relevance [17, 19]. This has been shown to not work reliably in a previous publication [19]. Therefore, caution is advised in attempting to apply subcooled liquid state data, such as those in Figure 1, to predicting vapor pressure behavior at ambient temperature conditions. That is, the use of Equation 6 to go from subcooled liquid estimates to sublimation vapor pressures is not always reliable, because of uncertainty in the subcooled liquid state property estimates. The data in Figure 2 are authentic sublimation data and should be of greater reliability in extrapolation to ambient conditions.

Tetrabromobisphenol-A and HBCD vapor pressures

The vapor pressures of TBBPA and HBCD were also compared with those of BDE209 (see Figure 3). The measurement temperatures were kept below the degradation temperature of TBBPA and HBCD, 528 K and 513 K, respectively [12,27]. The enthalpy of sublimation of HBCD is again seen to be close to that of BDE 209 (157.1 ± 3.5 kJ/mol), while the vapor pressure of HBCD is about 2 orders of magnitude higher than that of BDE209. The widely used TBBPA has a slightly higher vapor pressure than HBCD and octaBDE, and much higher than BDE209, but it has a slightly lower enthalpy of sublimation.

Thus, several of the more common BFRs have vapor pressures that are comparable to one another. It is not known if this vapor pressure property has direct bearing on their efficacy as flame retardants, though it is clear that to be effective, a flame retardant should allow the vaporization of a brominated species into a flame zone within a particular range of temperature.

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References

1. de Wit CA. An overview of brominated flame retardants in the environment. *Chemosphere*. 2002; 46:583–624. [PubMed: 11999784]
2. Rodan BD, Pennington DW, Eckley N, Boethling RS. Screening for persistent organic pollutants: Techniques to provide a scientific basis for POPs criteria in international negotiations. *Environ Sci Technol*. 1999; 33:3482–3488.

3. Streets SS, Henderson SA, Stoner AD, Carlson DL, Simcik MF, Swackhamer DL. Partitioning and bioaccumulation of PBDEs and PCBs in Lake Michigan. *Environ Sci Technol*. 2006; 40:7263–7269. [PubMed: 17180976]
4. Tokarz JA, Ahn MY, Leng J, Filley TR, Nies L. Reductive debromination of polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system. *Environ Sci Technol*. 2008; 42:1157–1164. [PubMed: 18351087]
5. Yen JH, Liao WC, Chen WC, Wang YS. Interaction of polybrominated diphenyl ethers (PBDEs) with anaerobic mixed bacterial cultures isolated from river sediment. *J Hazard Mater*. 2009; 165:518–524. [PubMed: 19019534]
6. Betts KS. New thinking on flame retardants. *Environ Health Persp*. 2008; 116:A210–A213.
7. Covaci A, Gerecke AC, Law RJ, Voorspoels S, Kohler M, Heeb NV, Leslie H, Allchin CR, de Boer J. Hexabromocyclododecanes (HBCDs) in the environment and humans: A review. *Environ Sci Technol*. 2006; 40:3679–3688. [PubMed: 16830527]
8. Johnson-Restrepo B, Adams DH, Kannan K. Tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDs) in tissues of humans, dolphins, and sharks from the United States. *Chemosphere*. 2008; 70:1935–1944. [PubMed: 18037156]
9. Shaw S. Halogenated Flame Retardants: Do the fire safety benefits justify the risks? *Rev Environ Health*. 2010; 25:261–306. [PubMed: 21268442]
10. Shi T, Chen SJ, Luo XJ, Zhang XL, Tang CM, Luo Y, Ma YJ, Wu JP, Peng XZ, Mai BX. Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. *Chemosphere*. 2009; 74:910–916. [PubMed: 19059630]
11. Schauer UMD, Volkel W, Dekant W. Toxicokinetics of tetrabromobisphenol A in humans and rats after oral administration. *Toxicol Sci*. 2006; 91:49–58. [PubMed: 16481339]
12. Barontini F, Cozzani V, Petarca L. Thermal stability and decomposition products of hexabromocyclododecane. *Ind Eng Chem Res*. 2001; 40:3270–3280.
13. Luda MP, Balabanovich AI, Hornung A, Camino G. Thermal degradation of a brominated bisphenol A derivative. *Polym Advan Technol*. 2003; 14:741–748.
14. Tittlemier SA, Halldorson T, Stern GA, Tomy GT. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. *Environ Toxicol Chem*. 2002; 21:1804–1810. [PubMed: 12206419]
15. Tittlemeier SA, Tomy GT. Vapor pressures of six brominated diphenyl ether congeners. *Environ Toxicol Chem*. 2001; 20:146–148. [PubMed: 11351402]
16. Wong A, Lei YD, Alaei M, Wania F. Vapor pressures of the polybrominated diphenyl ethers. *J Chem Eng Data*. 2001; 46:239–242.
17. Fu J, Suuberg EM. Vapor pressure of solid polybrominated diphenyl ethers determined via Knudsen effusion method. *Environ Toxicol Chem*. 2011; 30:2216–2219. [PubMed: 21766320]
18. Fu J, Rice JW, Suuberg EM. Phase behavior and vapor pressures of the pyrene + 9,10-dibromoanthracene system. *Fluid Phase Equilib*. 2010; 298:219–224.
19. Fu J, Suuberg EM. Solid vapor pressure for five heavy PAHs via the Knudsen effusion method. *J Chem Eng Data*. 2011; 43:1660–1665.
20. Oja V, Suuberg EM. Development of a nonisothermal Knudsen effusion method and application to PAH and cellulose tar vapor pressure measurement. *Anal Chem*. 1997; 69:4619–4626.
21. Goldfarb JL, Suuberg EM. The effect of halogen hetero-atoms on the vapor pressures and thermodynamics of polycyclic aromatic compounds measured via the Knudsen effusion technique. *J Chem Thermodyn*. 2008; 40:460–466. [PubMed: 20376299]
22. Bender R, Bieling V, Maurer G. The vapour pressures of solids: anthracene, hydroquinone, and resorcinol. *J Chem Eng Data*. 1983; 15:585–594.
23. Goldfarb JL, Suuberg EM. Vapor pressures and enthalpies of sublimation of ten polycyclic aromatic hydrocarbons determined via the Knudsen effusion method. *J Chem Eng Data*. 2008; 53:670–676.
24. Hansen PC, Eckert CA. An improved transpiration method for the measurement of very low vapor pressures. *J Chem Eng Data*. 1986; 31:1–3.

25. Sonnefeld WJ, Zoller WH, May WE. Dynamic coupled-column liquid-chromatographic determination of ambient-temperature vapor-pressures of polynuclear aromatic-hydrocarbons. *Anal Chem.* 1983; 55:275–280.
26. Pounder FE, Masson I. Thermal analysis, and its application to dinitrobenzenes. *J Chem Soc.* 1934:1357–1360.
27. Rzyman M, Grabda M, Oleszek-Kudlak S, Shibata E, Nakamura T. Studies on bromination and evaporation of antimony oxide during thermal treatment of tetrabromobisphenol A (TBBPA). *J Anal Appl Pyrol.* 2010; 88:14–21.

Figure 1. Effect of bromine content on the subcooled liquid state vapor pressure at 298.15 K ($P_{L, 298.15K}$) of polybrominated diphenyl ethers (PBDEs).

Figure 2. Sublimation vapor pressures of octabromodiphenyl ether (octaBDE) isomer mixture measured by using the Knudsen effusion method and comparing to sublimation vapor pressure of 4,4'-dibromodiphenyl ether (BDE15) and decabromodiphenyl ether (BDE209).

Figure 3. Sublimation vapor pressures of Tetrabromobisphenol-A (TBBPA), 1,2,5,6,9,10-hexabromocyclododecane (HBCD), and octaBDE isomer mixture measured by using the Knudsen effusion method and comparing to sublimation vapor pressure of decabromodiphenyl ether (BDE209).

Table 1

Melting temperatures and enthalpies of fusion of the brominated flame retardants (BFRs) examined in the present study

Compound	$T_{\text{fus}}(\text{K})$	$\Delta_{\text{fus}}H(\text{kJ/mol})$	Molecular structure
TBBPA	454.9 – 456.4	33.4
HBCD	449.2 – 451.9	30.12
OctaBDE mixture	409.2 – 433.2	27.2

TBBPA = tetrabromobisphenol A; HBCD = hexabromocyclododecane; octaBDEs = octabromodiphenyl ethers.

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)
TBBPA		HBCD	
389.0	0.00653	394.1	0.00228
394.1	0.0112	399.2	0.00517
399.1	0.0193	404.1	0.00814
404.0	0.0329	409.1	0.016
409.0	0.0545	414.1	0.0274
414.1	0.0924	419.1	0.0485
419.0	0.151	424.1	0.0805
424.0	0.251	427.1	0.106
429.0	0.404	429.1	0.126
434.1	0.640	434.1	0.185
439.1	1.00	439.1	0.285

TBBPA = tetrabromobisphenol A; HBCD = hexabromocyclododecane.

Table 3

Kundsen effusion method determined enthalpies of sublimation, vapor pressures at 298.15 K and slopes *B* and intercepts *A* of Equation 4 for the three brominated flame retardants (BFRs)

Compound	Temp range	$\Delta_{\text{sub}}H$ (kJ/mol)	<i>P</i> (Pa) (298.15K)	<i>B</i>	<i>A</i>
TBBPA	389 – 439	143.6 ± 0.4	8.47×10^{-9}	-7499.5	17.08
HBCD	394 – 439	153.7 ± 3.1	7.47×10^{-10}	-8028.0	17.80
OctaBDE mixture	384 – 406	150.8 ± 3.2	2.33×10^{-9}	-7878.0	17.79

TBBPA = tetrabromobisphenol A; HBCD = hexabromocyclododecane; octaBDEs = octabromodiphenyl ethers.