Vapor Pressures of the Polybrominated Diphenyl Ethers

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The supercooled liquid vapor pressures P_L of 23 polybrominated diphenyl ether congeners were determined as a function of temperature with a gas chromatographic retention time technique. P_L at 298.15 K ranged from 0.1 Pa for monobrominated diphenyl ethers to 10^{-6} Pa for heptabrominated diphenyl ethers. The halogen substitution pattern was found to influence PBDE vapor pressure, indicating that congeners with bromine substitutions in the ortho positions to the ether-link have higher vapor pressures. The enthalpy of vaporization $\Delta_{vap}H$ for the 23 PBDE congeners ranged from $(-67$ to $-116)$ kJ/mol, decreasing with each additional bromine substitution by about $(7$ to $8)$ kJ·mol^{-1}. $\Delta_{vap}H$ was also found to be influenced by the number of ortho bromines. Using a Junge–Pankow approach, the fraction of chemical adsorbed to aerosols as a function of temperature was estimated for three congeners and used to speculate on the likely environmental behavior of these chemicals.

Introduction

The polybrominated diphenyl ethers (PBDEs) (Figure 1) are a group of aromatic brominated compounds used in abundance as additive flame-retardants in polymers found in textiles and electrical appliances such as computers and televisions.[1] They are emerging as a significant class of environmental contaminants, having been detected in a wide range of environmental samples[2,3] and more recently in human milk, blood plasma, and adipose tissue.[4,5,6] Vapor pressures are indispensable in any attempt to quantify the release of PBDEs from polymer materials and to assess their environmental fate.

Despite the recent interest in these substances, basic physical–chemical property data are sparse, in particular on a congener-specific basis. Here we report the supercooled liquid vapor pressures P_L and the enthalpies of vaporization $\Delta_{vap}H$ for 23 PBDE congeners, determined with the gas chromatographic (GC) retention time technique by Bidleman.[7] A recent critical comparison of vapor pressure measurements, based on a statistical analysis of the data obtained with different methods and derived from 152 references, concluded that the indirect determination based on GC retention times "can be recommended as one of the most suitable [methods] for the determination of the vapor pressure of low volatility compounds".[8] The method is particularly suited to substances of low polarity, because the interactions of an apolar molecule with an apolar stationary GC phase such as poly(dimethylsiloxane) resemble the interactions between that molecule and its own pure liquid phase.[9] It is the only feasible method if only very small quantities of a compound are available, as is presently the case for individual PBDE congeners. The investigated set of chemicals includes the congeners most
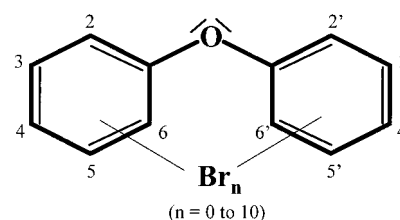

Figure 1. Structures of the polybrominated diphenyl ethers.

prevalent in environmental samples, most notably PBDE-47 and PBDE-99.

Methods

Chemicals. Cambridge Isotope Laboratories (Andover, MA) supplied the PBDE congeners. Polychlorinated biphenyls (PCBs) used for the calibration of the technique were obtained from Ultra Scientific, and the reference compound 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (p,p′-DDT) was from ChemService.

Instrumentation. A Hewlett-Packard 5890 gas chromatograph with an electron capture detector (ECD) and a dimethylpolysiloxane capillary column (0.32 mm i.d. × 1.0 m long, DB-1, J&W Scientific Columns, Folsom, CA) were used. The experiment was run isothermally at six or seven temperatures in the range (363.15 to 473.15) K, and the temperature of the GC oven was calibrated with a thermocouple prior to the beginning of the experiment. The injection port had a temperature of 523.15 K, and the ECD had a temperature of 573.15 K. The flow rate for the carrier gas (argon/methane) was approximately 4 mL·min^{-1}, and the split ratio was approximately 10:1.

Data Analysis. The procedure for deriving P_L of the PBDEs from GC retention times followed the method developed and described by Bidleman[7] and Hinckley et al.[9] Briefly, for each analyte a vapor pressure P_{GC} was calculated using

$$\ln(P_{GC}/Pa) = (\Delta_{vap}H/\Delta_{vap}H_{ref}) \ln(P_{L,ref}/Pa) + C \quad (1)$$

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Table 1. GC-Determined Vapor Pressures P_{GC} with Standard Deviations from Three Independent Determinations, Supercooled Liquid Vapor Pressure P_L at 298.15 K, Enthalpies of Vaporization $\Delta_{vap}H$, and Slopes m_L and Intercepts b_L of Eq 4 for 23 PBDE Congeners

ID[a]	compound	P_{GC}/Pa	P_L/Pa	$\Delta_{vap}H$/kJ·mol^{-1}	m_L	b_L
PBDE-1	2-monobromodiphenyl ether	0.160 ± 0.003	0.163	−63.7	−3327	10.37
PBDE-2	3-monobromodiphenyl ether	0.125 ± 0.002	0.128	−65.4	−3416	10.56
PBDE-7	2,4-dibromodiphenyl ether	0.0153 ± 0.0004	0.0168	−75.4	−3941	11.34
PBDE-8	2,4′-dibromodiphenyl ether	0.0124 ± 0.0002	0.0137	−76.4	−3991	11.42
PBDE-10	2,6-dibromodiphenyl ether	0.0256 ± 0.0005	0.0277	−73.1	−3818	11.25
PBDE-12	3,4-dibromodiphenyl ether	0.0107 ± 0.0003	0.0119	−77.4	−4020	11.56
PBDE-13	3,4′-dibromodiphenyl ether	0.0101 ± 0.0001	0.0113	−77.0	−4044	11.62
PBDE-15	4,4′-dibromodiphenyl ether	0.0088 ± 0.0001	0.00984	−78.0	−4071	11.65
PBDE-30	2,4,6-tribromodiphenyl ether	0.00396 ± 0.00005	0.00456	−85.1	−4232	11.85
PBDE-32	2,4′,6-tribromodiphenyl ether	0.0019 ± 0.0008	0.00225	−83.3	−4352	11.94
PBDE-33	2′,3,4-tribromodiphenyl ether	0.00149 ± 0.00003	0.00178	−81.0	−4443	12.15
PBDE-35	3,3′,4-tribromodiphenyl ether	0.00115 ± 0.00001	0.00139	−86.4	−4512	12.28
PBDE-37	3,4,4′-tribromodiphenyl ether	0.0008 ± 0.0003	0.00102	−86.7	−4528	12.20
PBDE-47	2,2′,4,4′-tetrabromodiphenyl ether	0.00025 ± 0.00001	0.000319	−92.0	−4805	12.62
PBDE-66	2,3′,4,4′-tetrabromodiphenyl ether	0.00019 ± 0.00001	0.000238	−93.5	−4882	12.75
PBDE-69	2,3′,4,6-tetrabromodiphenyl ether	0.00032 ± 0.00001	0.000400	−91.1	−4757	12.56
PBDE-75	2,4,4′,6-tetrabromodiphenyl ether	0.00039 ± 0.00001	0.000492	−90.1	−4706	12.48
PBDE-77	3,3,4,4′-tetrabromodiphenyl ether	0.000120 ± 0.000004	0.000156	−95.3	−4977	12.89
PBDE-82	2,2′,3,3′,4-pentabromodiphenyl ether	0.000048 ± 0.000001	0.0000647	−99.1	−5175	13.17
PBDE-99	2,2′,4,4′,5-pentabromodiphenyl ether	0.00005 ± 0.00003	0.0000682	−100.3	−5241	13.41
PBDE-115	2,3′,4,4′,6-pentabromodiphenyl ether	0.000022 ± 0.000001	0.0000302	−101.8	−5319	13.32
PBDE-153	2,2′,4,4′,5,5′-hexabromodiphenyl ether	0.0000058 ± 0.0000003	0.00000843	−107.6	−5620	13.78
PBDE-190	2′,3,3′,4,4′,5,6-heptabromodiphenyl ether	0.00000057 ± 0.00000008	0.000000905	−115.8	−6048	14.24

[a] ID numbers used follow the convention established by Ballschmiter et al.[16]

where $P_{L,ref}$ and $\Delta_{vap}H_{ref}$ refer to the well-established vapor pressure and enthalpy of vaporization of a standard reference compound. In this case, this compound was p,p′-DDT with a vapor pressure of $\log(P_L/\text{Pa}) = 12.48 - 4699.5(T/\text{K})^{-1}$. The ratio of the enthalpies and the constant C in eq 1 were obtained by plotting and linearly regressing the ratios of the measured isothermal GC retention times $t_R/t_{R,ref}$ at each temperature against the vapor pressure of the reference compound at that temperature using[7]

$$\ln(t_R/t_{R,ref}) = [1 - (\Delta_{vap}H/\Delta_{vap}H_{ref})] \ln(P_{L,ref}/\text{Pa}) - C \quad (2)$$

Equation 2 assumes that the infinite dilution activity coefficients in the stationary phase are the same for the analyte and the reference compound.[9] As this is an approximation, P_{GC} is not always identical to the vapor pressure of the (supercooled) liquid P_L, and a calibration of the method with closely related compounds is advisable.[7] This calibration involved eight PCB congeners for which vapor pressure is well-known from measurements based on the effusion and gas saturation techniques (see Table 1 in Lei et al.[10]). The calibration equation was

$$\log(P_{GC}/\text{Pa}) = 1.0368 \log(P_L/\text{Pa}) - 0.0239$$

$$r^2 = 0.9718 \quad (3)$$

Because the enthalpy of vaporization of the reference compound $\Delta_{vap}H_{ref}/\text{kJ·mol}^{-1}$ is known, $\Delta_{vap}H$ of the analytes can easily be derived from the enthalpy ratio obtained in the regression of eq 2.

   Previous studies[9] had shown that this method can determine the vapor pressures of nonpolar compounds within a factor of 2 of literature values, which is well within the precision of the classical techniques for low volatility compounds. Vapor pressures as low as those reported here are very difficult to determine with classical methods such as the saturator column and effusion technique.

Results

   Table 1 lists the measured vapor pressures P_{GC} and P_L of the 23 PBDE congeners at 298.15 K, as well as the
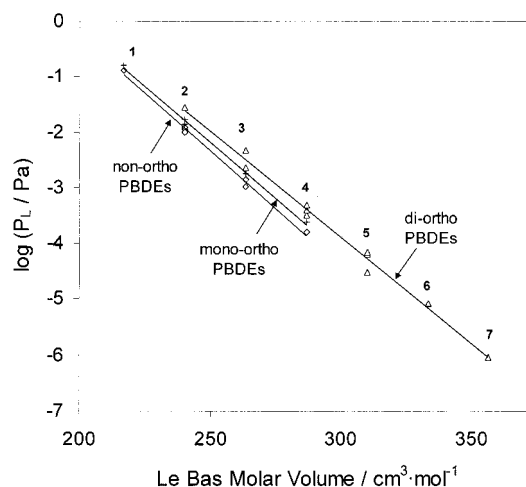

Figure 2. Relationship between vapor pressure, $\log P_L$ (Table 2), and Le Bas molar volume for 23 PBDE congeners with variable number of bromine substitutions in the ortho position to the ether group. The numbers indicate the total number of bromine substitutions. See text for linear regression equations and r^2.

intercepts b_L and slopes m_L of the temperature regressions:

$$\log(P_L/\text{Pa}) = m_L/(T/\text{K}) + b_L \quad (4)$$

Enthalpies of vaporization $\Delta_{vap}H$ are also listed. The values for P_{GC} were highly reproducible, as is evident from the small standard deviations derived from three independent determinations.

Discussion

   Relationship between $\log P_L$ and Molecular Size and Substitution Pattern. Figure 2 shows the relationship between vapor pressure $\log P_L$ and the molar volume V_M for the 23 PBDE congeners whose P_L values were measured in this study. The molar volumes of the PBDEs were estimated using the method by Le Bas.[11] Clearly, the vapor pressure decreases linearly with increasing size of

the molecule. Each additional bromine substitution causes a drop in vapor pressure of the PBDEs by a factor of 6 to 9.

The Le Bas molar volume is identical for a homologue group; that is, it does not distinguish among diphenyl ethers with the same number of bromine substitutions. However, the measured vapor pressures within a homologue group, such as the tri- and tetrabromodiphenyl ethers, can range over half an order of magnitude. Closer examination of the data revealed that within a homologue group the vapor pressure increases with the number of bromine substitutions in the ortho positions to the ether link (2, 2′, 6, 6′). A similar dependence of vapor pressure on the halogen substitution pattern has been noted for the PCBs[12] and was explained by the distortion from planarity between the two aromatic rings caused by multiple halogen substitutions in the ortho positions. The data presented here suggested that a similar effect may be occurring for the brominated diphenyl ethers. On average, the addition of a bromine in one of the ortho positions increased vapor pressure by approximately 0.2 log units. A similar analysis using data reported by Kurz and Ballschmiter[13] indicated that the chlorine substitution pattern has a similar effect on the vapor pressure of polychlorinated diphenyl ethers (PCDEs), although it was less pronounced than for the PBDEs. In contrast to the case of the PCBs, this effect cannot be explained by a lack of planarity, because even in the absence of halogen substitutions the diphenyl ether structure is nonplanar. The bulky halogens in the 2,2′,6,6′ positions obviously cause subtle differences in three-dimensional molecular structure or polarity that result in weaker intermolecular interactions in the pure substance and thus slightly higher vapor pressure.

Individual regressions between log P_L and V_M were calculated for the non-ortho, mono-ortho, and di-ortho PBDEs, and the respective regression curves are included in Figure 2.

$$\log(P_L/\text{Pa}) = -0.0415\,V_M/\text{cm}^3\cdot\text{mol}^{-1} +$$
$$8.044 \text{ for non-ortho PBDEs} \qquad r^2 = 0.995 \quad (5)$$

$$\log(P_L/\text{Pa}) = -0.0403\,V_M/\text{cm}^3\cdot\text{mol}^{-1} +$$
$$7.905 \text{ for mono-ortho PBDEs} \qquad r^2 = 0.998 \quad (6)$$

$$\log(P_L/\text{Pa}) = -0.0381\,V_M/\text{cm}^3\cdot\text{mol}^{-1}$$
$$+ 7.548 \text{ for di-ortho PBDEs} \qquad r^2 = 0.991 \quad (7)$$

Estimation of Vapor Pressure for Additional Congeners from Relative Retention Times. Sjödin et al.[14] recently reported relative retention times, RRTs (vs dechlorane 603), on four different GC columns for 31 PBDE congeners, including 17 congeners for which vapor pressure was measured in this study. The log P_L and RRTs on the apolar CPSil-8 column were highly correlated, the linear regression equations being

$$\log(P_L/\text{Pa}) = -7.573(\text{RRT}) +$$
$$1.184 \text{ for non-ortho PBDEs} \qquad r^2 = 0.995 \quad (8)$$

$$\log(P_L/\text{Pa}) = -7.701(\text{RRT}) +$$
$$1.294 \text{ for mono-ortho PBDEs} \qquad r^2 = 0.999 \quad (9)$$

$$\log(P_L/\text{Pa}) = -6.728(\text{RRT}) +$$
$$0.744 \text{ for di-ortho PBDEs} \qquad r^2 = 0.998 \quad (10)$$

The RRT reported for PBDE-190[14] was not used in the

Table 2. Vapor Pressures for Seven PBDE Congeners Derived Using Regressions between log P_L and Relative Retention Times on a CPSil-8 Column Reported by Sjödin et al.[14]

ID[a]	compound	P_L/Pa
PBDE-17	2,2′,4-tribromodiphenyl ether	0.00219[b]
PBDE-25	2,3′,4-tribromodiphenyl ether	0.00201[c]
PBDE-28	2,4,4′-tribromodiphenyl ether	0.00160[c]
PBDE-71	2,3′,4′,6-tetrabromodiphenyl ether	0.000410[b]
PBDE-85	2,2′,3,4,4′-pentabromodiphenyl ether	0.0000281[b]
PBDE-116	2,3,4,5,6-pentabromodiphenyl ether	0.0000499[b]
PBDE-119	2,3′,4,4′,6-pentabromodiphenyl ether	0.0000807[b]

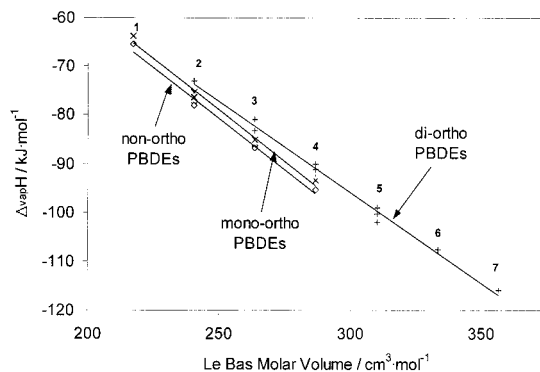[a] ID numbers used follow the convention established by Ballschmiter et al.[16] [b] Using eq 9. [c] Using eq 10.

Figure 3. Relationship between enthalpies of vaporization, $\Delta_{vap}H$, and Le Bas molar volume for 23 PBDE congeners. The numbers indicate the total number of bromine substitutions. See text for linear regression equations and r^2.

calculation of regression eq 10, because it appeared unreasonably long, suggesting a misidentification. We used these equations to estimate P_L for seven additional congeners for which RRT had been reported by Sjödin et al.[14] These data are reported in Table 2. To avoid errors associated with extrapolations, we refrained from predicting P_L for congeners with more than two ortho bromines and for congeners with a RRT larger than that of the PBDE-153.

Comparison of P_L Values of PBDEs with Those of Other Halogenated Aromatic Compounds. When the log P_L versus V_M relationships of the PBDEs were compared with those for several other groups of halogenated aromatic compounds, such as the PCDEs,[13] the PCBs,[12] and the PCNs,[10] it was apparent that the PBDEs have relatively low vapor pressures compared to those of chlorinated compounds of similar molar volume. However, when compared to chlorinated compounds of similar molecular mass, the PBDEs are much more volatile. This can be explained by the fact that a bromine substitution adds substantially more mass to a molecule than a chlorine substitution, but only marginally more volume. As a result, PBDEs tend to be more volatile than might be expected from a comparison of their molecular mass with that of chlorinated aromatic compounds. The slopes of the log P_L versus V_M relationships for the PBDEs are slightly steeper than those of the coplanar PCBs but much steeper than those for the multi-ortho-PCBs, PCDEs, and PCNs.

Relationship between $\Delta_{vap}H$ and Molecular Size. Figure 3 shows the relationship between the enthalpy of vaporization and the Le Bas molar volume for the 23 PBDE congeners. Again, the variable number of bromine atoms in the ortho position to the ether link can explain much of the variability of $\Delta_{vap}H$ within a homologue group. The

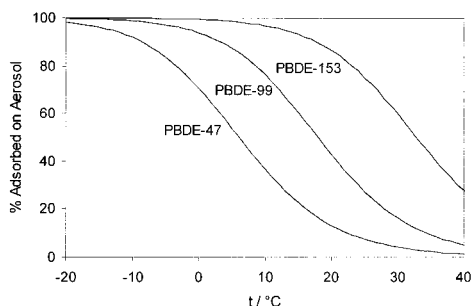**Figure 4.** Estimated fraction of congeners PBDE-47, PBDE−99, and PBDE−153 adsorbed to aerosol as a function of temperature.

regression equations are

$$\Delta_{vap}H/\text{kJ·mol}^{-1} = -0.418\,V_M/\text{cm}^3\text{·mol}^{-1} +$$
$$23.701 \text{ for non-ortho PBDEs} \qquad r^2 = 0.990 \quad (11)$$

$$\Delta_{vap}H/\text{kJ·mol}^{-1} = -0.418\,V_M/\text{cm}^3\text{·mol}^{-1} +$$
$$25.582 \text{ for mono-ortho PBDEs} \qquad r^2 = 0.989 \quad (12)$$

$$\Delta_{vap}H/\text{kJ·mol}^{-1} = -0.369\,V_M/\text{cm}^3\text{·mol}^{-1} +$$
$$15.004 \text{ for di-ortho PBDEs} \qquad r^2 = 0.992 \quad (13)$$

Aerosol−Vapor Partitioning. The environmental fate of an organic chemical is strongly influenced by its partitioning characteristics. Atmospheric behavior in particular is determined by the distribution between gas and aerosol phase.[15] The Junge−Pankow relationship describes this phase equilibrium as a function of P_L:

$$\Phi = cS_T/(P_L + cS_T) \qquad (14)$$

where Φ is the fraction of chemical sorbed to aerosols, c is a contaminant- and aerosol-specific parameter, and S_T is the total surface area of the aerosols. Assuming that this relationship is applicable to the PBDEs, that c has a value of 0.172 Pa·m, and that the total aerosol surface area S_T is 1.5×10^{-4} m^2/m^3, typical of continental background air,[12,15] we can estimate Φ for selected PBDE congeners in the environmental temperature range (Figure 4).

This estimation indicated that PBDE-153, and likely all other PBDEs with six and more bromine substitutions, are essentially particle-bound substances at typical atmospheric temperatures. Tri- to pentabrominated diphenyl ethers can be expected to partition significantly to aerosols, but can also occur in the gaseous state at warm air temperatures and may thus be transported further away from source areas. The PBDEs with two or less bromines should be mostly gaseous contaminants and, if sufficiently stable, may have the potential for significant long-range transport.

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