

Determination of Vaporization Enthalpies of Polychlorinated Biphenyls by Correlation Gas Chromatography

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The vaporization enthalpies of 16 polychlorinated biphenyls have been determined by correlation gas chromatography. This study was prompted by the realization that the vaporization enthalpy of the standard compounds used in previous studies, octadecane and eicosane, were values measured at 340 and 362 K, respectively, rather than at 298 K. Adjustment to 298 K amounts to a 7–8 kJ/mol increment in the values. With the inclusion of this adjustment, vaporization enthalpies evaluated by correlation gas chromatography are in good agreement with the values determined previously in the literature. The present results are based on the vaporization enthalpies of several standards whose values are well established in the literature. The standards include a variety of *n*-alkanes and various chlorinated hydrocarbons. The vaporization enthalpies of PCBs increased with the number of chlorine atoms and were found to be larger for meta- and para-substituted polychlorinated biphenyls.

Polychlorinated biphenyls (PCBs), a class of persistent organic chemicals, have been a source of environmental concern. The same physicochemical properties of PCBs, namely, inflammability, chemical stability, and lipophilicity, which contributed to the widespread use of these compounds in industrial applications, are also partially responsible for their designation as environmental pollutants.¹

The migration of PCBs in the environment can be modeled by gas chromatographic separation. In gas chromatography, components of a mixture are volatilized into a carrier gas that passes through a column; different components of the mixture move at different rates, elute separately, and can be identified.² Similarly, PCBs with different volatilities migrate through the global atmosphere at different velocities. Highly volatile PCBs tend to remain airborne and migrate faster. Less volatile PCBs are more prone to partition into soil or vegetation.² Most PCBs are solid at ambient temperatures. However, for many environmental applications, the subcooled liquid vapor pressures and the corresponding vaporization enthalpies are the relevant thermodynamic properties associated with the dispersal of PCBs.^{3,4}

Gas saturation^{5,6} and effusion⁷ have been used to determine the vapor pressure and vaporization enthalpy of numerous PCBs. Gas chromatography has been widely used to determine the vapor pressure of PCBs in the presence of different standards such as isobutyl 2,4,5-trichlorophenoxyacetate,⁸ eicosane and octadecane,⁹ *p,p'*-DDT,¹⁰ and octachloronaphthalene.^{11,12} Gas chromatography has several advantages over other methods; these include speed, tolerance to relatively impure compounds, and small sample size requirement.⁸

In the literature, the vaporization enthalpies ($\Delta_{\text{vap}}H_{\text{m}}$) of most PCBs at 298.15 K have been measured in the presence of one or two standards. In the work reported by Bidleman,⁹ the reference compounds used were octadecane for more volatile PCBs and eicosane for less volatile PCBs. The accuracy of the results for test compounds depends on the accuracy of the vaporization enthalpies of the reference compounds. The value used by Bidleman for the vaporization enthalpy of octadecane was 84.5 kJ/mol at 340 K; the value used for eicosane was 93.4 kJ/mol at 362 K. The vaporization enthalpies of these two standard compounds at 340 and 362 K, respectively, were used to calculate the vaporization enthalpies of 32 PCBs at 298.15 K.¹³ More recently, Ruzicka and Majer¹⁴ recommended the following vaporization enthalpies at 298.15 K for octadecane and eicosane:

$$\text{octadecane } \Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) = 91.4 \text{ kJ/mol}$$

$$\text{eicosane } \Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) = 101.8 \text{ kJ/mol}$$

A comparison of the recommended values of $\Delta_{\text{vap}}H_{\text{m}}$ at 298.15 and 340 K reveals a difference of ~ 7 kJ/mol for octadecane. A

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difference of 8 kJ/mol was observed in the value of $\Delta_{\text{vap}}H_{\text{m}}$ for eicosane at 298.15 and 362 K. In view of the large discrepancy in the recommended values at 298.15 K and the values used by Bidleman, and the fact that many of the vaporization enthalpies reported for PCBs are based on the values of two standards, we decided to reexamine the vaporization enthalpies of a representative number of PCBs. The measurements reported in this work are based on the technique of correlation gas chromatography.

Correlation gas chromatography utilizes the correlation observed between the vaporization enthalpy of several standards and their enthalpy of transfer from solution in the GC stationary phase to the gas phase as measured by gas chromatography. The enthalpy of transfer from solution in the GC stationary phase to vapor phase ($\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$) is measured by gas chromatography from the temperature dependence of the retention time. The corrected retention time, t_r , for each compound is calculated from the difference between the retention times of the solute and the unretained reference, usually the solvent. Since the viscosity of helium increases with increasing column temperature, the retention time of the solvent increases while that of the other solutes decreases.¹⁵ This is a good indication of whether the solvent is truly unretained at the temperature of the experiment. The corrected retention time measures the time each component spends on the column, and it is inversely proportional to the vapor pressure of the compound on the stationary phase of the column.¹⁶ Since each solute presumably dissolves in the stationary phase, $\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$ values can be measured for both solids and liquids.

EXPERIMENTAL SECTION

Instrumental Information. All experiments were performed on a Hewlett-Packard model 5890 Series II gas chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector. The retention times, in minutes, were recorded by a Hewlett-Packard model 3396A integrator/plotter. The columns utilized for chromatography were 15 m \times 0.25 mm SPB-5 (from Supelco, Bellefonte, PA) and 30 m \times 0.25 mm SPB-5 dimethylsiloxane capillary columns, each with 0.25- μm film thickness. Helium was used as the carrier gas, with column head pressure of 48 or 68 kPa. The column temperature was monitored independently using a Fluke 51 K/J thermometer. Constant temperature was maintained within ± 0.1 °C. The temperature measured in degree Celsius was adjusted to SI units of temperature by the addition of 273.15 K. Retention time measurements were conducted over a 25–30 K temperature interval. Five minutes was allowed for equilibration at each temperature. The detector and injector were maintained at 250 and 200 °C, respectively, for more volatile PCBs; both detector and injector were kept at 300 °C for less volatile PCBs (trichlorobiphenyls and higher homologues). Polychlorinated biphenyls were purchased from Accustandard (New Haven, CT) or were kindly provided by Dr. T. F. Bidleman (University of Toronto, Canada).

Procedure. A small amount of the sample was added to ~ 1 mL of methylene chloride. Analyses were performed using a split injection ratio of $\sim 100:1$. A split injection was used to keep sample loading to a minimum, thereby also minimizing solute–solute

interactions and increasing the accuracy of the retention time measurement.¹⁵ The standard size of injection was 0.5 μL . The purity of the samples was 99%. To ensure that the vaporization enthalpies were not dependent on one set of standards, different combinations of PCBs and standard compounds were examined under different experimental conditions (Supporting Information, Table 1).

A plot of $\ln(1/t_r)$ against $(1/T)$, similar to the Clausius–Clapeyron plot of $\ln(p)$ against $(1/T)$, results in a straight line whose slope is, by analogy, $-(\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}})/R$, where R is the gas constant.¹⁶ The vaporization enthalpy of the target compound is calculated from the equation of the line obtained from the plot of $\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$ against $\Delta_{\text{vap}}H_{\text{m}}$ (literature, 298.15 K) for the reference compounds. For certain standards, the vaporization enthalpy at 298.15 K is not directly available in the literature. For example, for 1-chlorohexadecane, only the vapor pressures in the temperature range 438.75–470.35 K have been reported in the literature.¹⁷ A plot of $\log(p/\text{Pa})$ against $1/(T/\text{K})$ was used to determine the enthalpy of vaporization from the product of the slope and the gas constant, $R = 8.314 \text{ J/K}\cdot\text{mol}$. The resulting vaporization enthalpy at the mean temperature, T_{mean} , was corrected to 298.15 K using the following equation:¹⁸

$$\Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{vap}}H_{\text{m}}(T_{\text{mean}}) + [10.58 + 0.26 \{C_{p1 \text{ estd}}(298.15 \text{ K})\}] \{T_{\text{mean}} - 298.15\}$$

The value of the heat capacity of the liquid phase, $C_{p1 \text{ estd}}(298.15 \text{ K})$, was estimated using a group additivity method.¹⁹

RESULTS AND DISCUSSION

The compounds and experimental conditions for each mixture analyzed by correlation gas chromatography are presented in Supporting Information, Table 1.

A plot of $\ln(1/t_r)$ as a function of $(1/T)$ for each compound in each of the 18 mixtures yielded a straight line, as illustrated for mixture 13 in Figure 1. The slope of the plot for each compound in mixture 13 is given in the second column of Table 1. The enthalpy of transfer from solution in the GC stationary phase to vapor ($\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$) was determined from the product of the slope and the gas constant. The correlation between the literature values of vaporization enthalpies at 298.15 K ($\Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K})$) with $\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$ for the reference compounds in mixture 13 is illustrated in Figure 2. The uncorrected retention times of each compound in each mixture, the correlation coefficient, the slope of the plot of $\ln(1/t_r)$ vs $(1/T)$, and $\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$ are given in Supporting Information, Table 2. All plots were characterized by correlation coefficients (r^2) greater than 0.99. The regression equation for the plot of $\Delta_{\text{soln}}^{\text{vap}}H_{\text{m}}$ (correlation GC) against $\Delta_{\text{vap}}H_{\text{m}}$ (literature, 298.15 K) for each mixture is presented in Supporting Information, Table 3.

The results from mixtures 4, 6, and 13 demonstrate that a good correlation is obtained between enthalpies of transfer and the literature vaporization enthalpies for mixtures containing n -alkanes and both mono- and polychlorinated standards. This correlation

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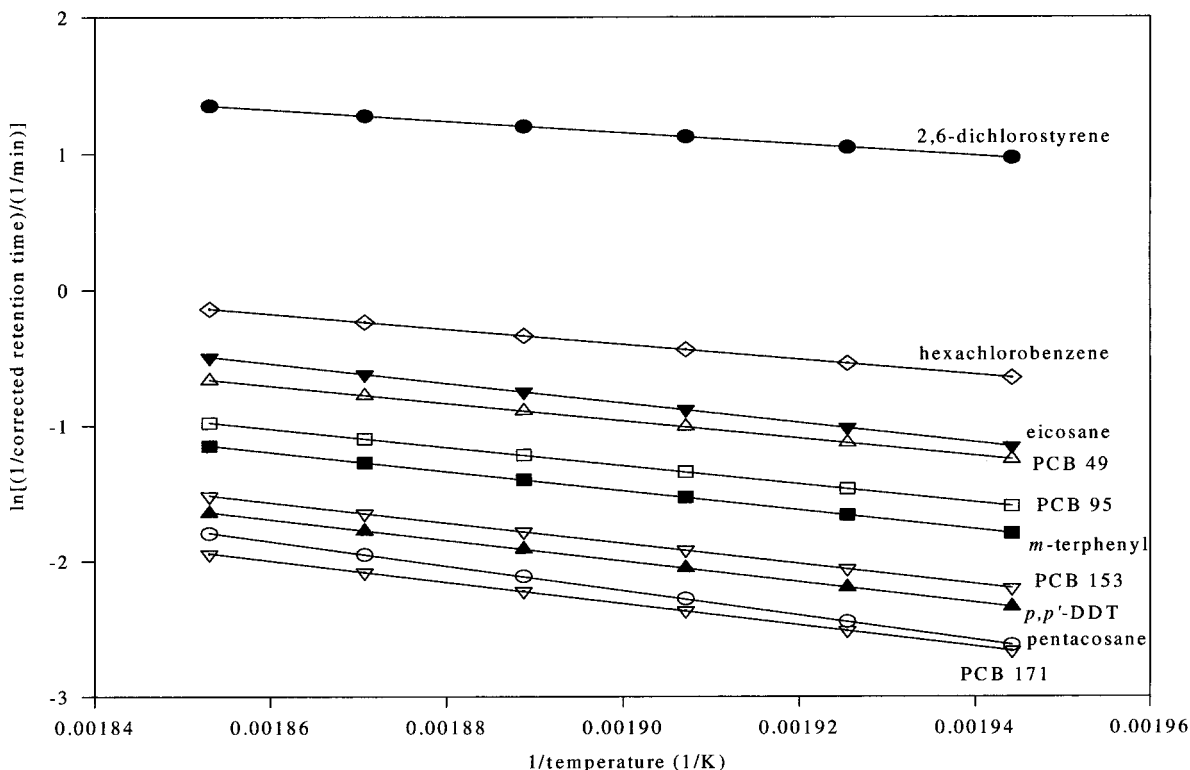


Figure 1. Plot of $\ln(1/\text{corrected retention time})/(1/\text{min})$ against $(1/\text{temperature}) (1/\text{K})$ for mixture 13.

Table 1. Correlation Data for Mixture 13

compounds	slope	$\Delta_{\text{soln}}^{\text{vap}}H_m$ (correlation GC), kJ/mol	$\Delta_{\text{vap}}H_m$ (298.15 K), kJ/mol	
			literature	calcd from regression eq
2,6-dichlorostyrene	-4176	34.7	53.0 ^a	52.3
hexachlorobenzene	-5569	46.3	72.3 ^b	73.7
<i>p,p'</i> -DDT	-7642	63.5	106.0 ^c	105.6
<i>m</i> -terphenyl	-7070	58.8	95.1 ^d	96.8
eicosane	-7227	60.1	101.8 ^e	99.2
pentacosane	-9049	75.2	126.9 ^f	127.3
2,2',4,5'-tetrachlorobiphenyl	-6418	53.4		86.8
2,2',3,5',6-pentachlorobiphenyl	-6747	56.1		91.9
2,2',4,4',5,5'-hexachlorobiphenyl	-7494	62.3		103.4
2,2',3,3',4,4',6-heptachlorobiphenyl	-7869	65.4		109.1

^a From ref 21. ^b From ref 22. ^c From ref 23. ^d From ref 24. ^e From ref 14. ^f From ref 25. Regression equation: $\Delta_{\text{vap}}H_m$ (298.15 K) = 1.851($\Delta_{\text{soln}}^{\text{vap}}H_m$) - 11.99. Correlation coefficient: 0.9963.

has been extremely important in the analysis of the higher homologues of PCBs since reference compounds with a high degree of chlorination, whose retention times do not overlap with the retention times of the PCBs being examined, are generally unavailable. The vaporization enthalpies of larger hydrocarbons served as standards in the evaluation of the highly chlorinated PCBs. A summary of the vaporization enthalpies determined from the correlation between $\Delta_{\text{vap}}H_m$ (298.15 K) and $\Delta_{\text{soln}}^{\text{vap}}H_m$ for each compound in each mixture is given in Table 2.

The results in Table 2 demonstrate that the values of $\Delta_{\text{vap}}H_m$ (298.15 K) calculated from the correlation equations are in good agreement with the reported literature values. In most cases, the difference between the calculated vaporization enthalpies and the literature values is within the normal error associated with the determination of vaporization enthalpy. This has been demonstrated by 1-chlorohexadecane, which has been used in 12 different mixtures. The average calculated value of the vaporization

enthalpy of 1-chlorohexadecane in this study was 96.4 ± 0.9 kJ/mol, compared to the literature value of 98.0 kJ/mol.¹⁷ In general, there is excellent agreement between calculated and experimental vaporization enthalpies for chlorinated and hydrocarbon standards used in the same mixture.

Harner and Bidleman²⁰ calculated the enthalpy of transfer of PCBs from octanol to the vapor phase ($\Delta_{\text{oct}}^{\text{air}}H$) and K_{OA} , the equilibrium constant associated with this transfer. The values of $\Delta_{\text{oct}}^{\text{air}}H$ were compared to $\Delta_{\text{vap}}H_m$ reported by Falconer and Bidleman.¹³ It was reported by Harner and Bidleman that, on average, $\Delta_{\text{oct}}^{\text{air}}H$ was 6.6 kJ/mol lower than $\Delta_{\text{vap}}H_m$. However, a comparison of our values of vaporization enthalpies ($\Delta_{\text{vap}}H_m$

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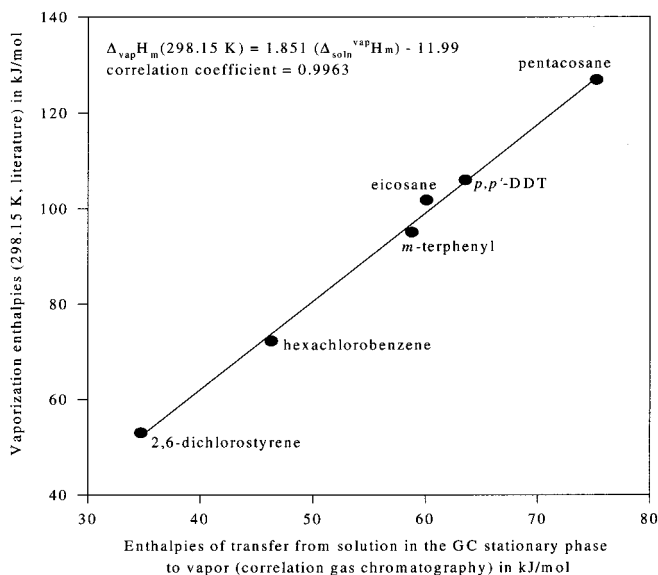


Figure 2. Correlation of vaporization enthalpies (298.15 K, literature) against enthalpies of transfer from solution in the GC stationary phase to vapor for the reference compounds in mixture 13.

(298.15 K, correlation GC)) for five compounds and $\Delta_{\text{ocl}}^{\text{air}}H$ from Harner and Bidleman²⁰ results in a difference of 11.0 kJ/mol, compared to 2.6 kJ/mol using Falconer and Bidleman's $\Delta_{\text{vap}}H_m$ values. This will affect the enthalpy of dissolution of the liquid-phase PCBs in octanol, $\Delta_{\text{sol}}H$, as calculated by Harner and Bidleman²⁰ from the difference between the values of $\Delta_{\text{ocl}}^{\text{air}}H$ and $\Delta_{\text{vap}}H_m$. Hence, the larger vaporization enthalpies determined in this study will influence the estimation of other significant physicochemical properties of polychlorinated biphenyls.

A comparison of the vaporization enthalpies determined by correlation gas chromatography and the literature values is depicted in Table 3. The third column in Table 3 represents the results from our analysis of PCBs. However, if the values of $\Delta_{\text{vap}}H_m$ (298.15 K) for octadecane and eicosane, reported by Ruzicka and Majer,¹⁴ are used to correct the vaporization enthalpies of PCBs reported by Falconer and Bidleman,¹³ the results are in good agreement with the values determined by our study. The last column in Table 3 represents these corrected values.

The vaporization enthalpy of PCBs increases with the number of chlorine atoms on the biphenyl ring. PCBs that are substituted at the meta and para positions are more nearly coplanar compared

Table 2. Summary of the Correlation GC and Literature Values of $\Delta_{\text{vap}}H_m$ (kJ/mol) at 298.15 K for All Compounds

compounds	no. of measrmts	$\Delta_{\text{vap}}H_m$ (298.15 K)	
		correlation GC ^a	literature
1-chloronaphthalene	6	64.0 ± 0.3	64.5 ^{b,c}
1-chlorododecane	6	64.0 ± 0.2	64.0 ^{b,d}
1-chlorododecane	10	73.9 ± 1.4	75.0 ^{b,e}
1-chlorohexadecane	12	96.4 ± 0.9	98.0 ^{b,f}
2,6-dichlorostyrene	8	53.8 ± 1.5	53.0 ^{b,g}
p,p'-DDT	6	106.1 ± 1.3	106.0 ^{b,h}
hexachlorobenzene	4	74.4 ± 0.7	72.3 ^{b,i}
dodecane	3	62.1 ± 0.2	61.5 ^j
tetradecane	3	72.1 ± 0.0	71.7 ^j
octadecane	5	91.3 ± 2.9	91.4 ^k
eicosane	8	102.8 ± 2.2	101.8 ^k
tricosane	2	118.7 ± 0.0	120.5 ^j
pentacosane	4	128.6 ± 2.2	126.9 ^j
hexacosane	2	136.4 ± 0.2	139.1 ^j
biphenyl	4	64.5 ± 2.2	65.6 ^l
m-terphenyl	4	97.2 ± 0.3	95.0 ^{b,m}
anthracene	2	79.1 ± 0.0	77.9 ⁿ
1 ^o	2	72.1 ± 2.0	
2	2	74.3 ± 1.1	
3	8	71.6 ± 0.7	
7	4	75.4 ± 1.5	
9	2	76.8 ± 0.4	
11	2	81.0 ± 0.2	
15	2	81.4 ± 0.3	
18	4	80.2 ± 0.9	
49	2	87.4 ± 0.8	
53	4	84.9 ± 0.6	
95	2	92.3 ± 0.6	
96	2	89.6 ± 0.2	
103	2	91.6 ± 0.5	
153	2	103.5 ± 0.1	
156	2	112.6 ± 0.4	
171	2	109.1 ± 0.0	

^a The vaporization enthalpies ($\Delta_{\text{vap}}H_m$) are average values that have been calculated from the regression equation from each correlation GC experiment. The uncertainties represent the standard deviation.

^b A plot of $\log(p/\text{Pa})$ against $1/(T/\text{K})$ was used to determine the enthalpy of vaporization from the product of the slope and the gas constant, $R = 8.314 \text{ J/K}\cdot\text{mol}$. The vaporization enthalpy at the mean temperature, T_{mean} , was corrected to 298.15 K using the following equation:¹⁸ $\Delta_{\text{vap}}H_m(298.15 \text{ K}) = \Delta_{\text{vap}}H_m(T_{\text{mean}}) + [10.58 + 0.26\{C_p^{\text{estd}}(298.15 \text{ K})\} \{T_{\text{mean}} - 298.15\}]$. The value of the heat capacity of the liquid phase, $C_p^{\text{estd}}(298.15 \text{ K})$, was estimated using a group additivity method.¹⁹ ^c The vaporization enthalpy at the mean temperature of 368 K was given in ref 26. ^d Temperature range/K: 359.35–385.95 from ref 17. ^e Temperature range/K: 389.15–426.85 from ref 17. ^f Temperature range/K: 438.75–470.35 from ref 17. ^g Temperature range/K: 321–351 from ref 21. ^h From ref 23. Temperature range/K: (a) 343.15–453.15, (b) 383.15–413.15. The average of the values from (a) and (b) was used. ⁱ Temperature range/K: 387.55–439.55 from ref 22. ^j From ref 25. ^k From ref 14. ^l From ref 27. ^m The vaporization enthalpy at the mean temperature of 477 K was given in ref 24. ⁿ From ref 28. ^o The number refers to the IUPAC designation of PCBs.

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to ortho-substituted polychlorinated biphenyls. This results in stronger intermolecular interactions, which leads to lower vapor pressure and higher vaporization enthalpy for meta- and para-substituted PCBs. Within the pentachlorobiphenyl homologue, isomers 95 (2,2',3,5',6-pentachlorobiphenyl) and 103 (2,2',4,4',5,6-pentachlorobiphenyl) have comparable vaporization enthalpies of 92.3 and 91.6 kJ/mol, respectively. However, isomer 96 (2,2',3,6,6'-pentachlorobiphenyl) has a lower vaporization enthalpy of 89.6 kJ/mol. Isomer 96 has four ortho chlorine atoms compared to three ortho chlorine atoms on isomers 95 and 103. Similarly, 2,3,3',4,4',5-hexachlorobiphenyl (PCB 156) has a higher vaporization enthalpy compared to 2,2',4,4',5,5'-hexachlorobiphenyl (PCB

Table 3. Comparison of Vaporization Enthalpies of PCBs Determined by Correlation GC (Average Values) and Values Reported in the Literature^{9,13}

IUPAC no.	compounds	$\Delta_{\text{vap}}H_m$, kJ/mol		
		correlation GC (this study)	Bidleman's original values ^a	Bidleman's values corrected to 298.15 K
1	2-monochlorobiphenyl	72.1	64.45	70.00
2	3-monochlorobiphenyl	74.3	66.56	72.29
3	4-monochlorobiphenyl	71.6	66.79	72.54
7	2,4-dichlorobiphenyl	75.4	73.54	79.88
9	2,5-dichlorobiphenyl	76.8	73.95	80.31
11	3,3'-dichlorobiphenyl	81.0	75.36	81.85
15	4,4'-dichlorobiphenyl	81.4	76.03	82.58
18	2,2',5-trichlorobiphenyl	80.2	na ^b	
49	2,2',4,5'-tetrachlorobiphenyl	87.4	na	
53	2,2',5,6'-tetrachlorobiphenyl	84.9	78.77	85.55
95	2,2',3,5',6-pentachlorobiphenyl	92.3	na	
96	2,2',3,6,6'-pentachlorobiphenyl	89.6	na	
103	2,2',4,5',6-pentachlorobiphenyl	91.6	na	
153	2,2',4,4',5,5'-hexachlorobiphenyl	103.5	91.43	99.30
156	2,3,3',4,4',5-hexachlorobiphenyl	112.6	94.76	102.92
171	2,2',3,3',4,4',6-heptachlorobiphenyl	109.1	95.89	104.14

^a Bidleman's original values were reported to four significant figures. ^b na, not available.

153) and 2,2',3,3',4,4',6-heptachlorobiphenyl (PCB 171) due to the presence of four meta and para chlorine atoms on the biphenyl ring of PCB 156.

CONCLUSIONS

Correlation gas chromatography is a fast and reliable method of evaluating vaporization enthalpies because it is based on the vaporization enthalpies of several standard compounds whose values are well established in the literature. The vaporization enthalpies of PCBs at 298.15 K in this study are considerably larger than the values reported in the literature. The difference is primarily due to the failure to adjust the vaporization enthalpies of the standard compounds, octadecane and eicosane, to 298.15 K. With the inclusion of this adjustment, values determined in this study are in good agreement with the enthalpies of vaporization reported in the literature.

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SUPPORTING INFORMATION AVAILABLE

The compounds and experimental conditions for each mixture analyzed by correlation gas chromatography are presented in Table 1. The uncorrected retention times, correlation coefficient, the slope of the plot of $\ln(1/t_r)$ vs $(1/T)$, and $\Delta_{\text{soln}}^{\text{vap}}H_m$ for each compound in each mixture are given in Table 2. The regression equations for the plot of $\Delta_{\text{soln}}^{\text{vap}}H_m$ (correlation GC) against $\Delta_{\text{vap}}H_m$ (literature, 298.15 K) for the standard compounds in each mixture are presented in Table 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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