J. Chem. Eng. Data 1990, 35, 232-237

Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data

Daniel A. Hinckley,[†,‡] **Terry F. Bidleman,***[,†,§,⊥] **and William T. Foreman**[§,∥]

Marine Science Program, Department of Chemistry, and Belle W. Baruch Institute for Marine Biology and Coastal Research, University of South Carolina, Columbia, South Carolina 29208

Jack R. Tuschall[#]

Northrop Services, Inc., P.O. Box 12313, Research Triangle Park, North Carolina 27709

Vapor pressures for nonpolar and moderately polar organochlorine, pyrethroid, and organophosphate insecticides, phthalate esters, and organophosphate flame retardants were determined by capillary gas chromatography (GC). Organochlorines and polycyclic aromatic hydrocarbons with known liquid-phase vapor pressures ($P°_L$) (standard compounds) were chromatographed along with two reference compounds n-C_{20} (eicosane) and p,p'-DDT on a 1.0-m-long poly(dimethylsiloxane) bonded-phase (BP-1) column to determine their vapor pressures by GC ($P°_{GC}$). A plot of log $P°_L$ vs log $P°_{GC}$ for standard compounds was made to establish a correlation between measured and literature values, and this correlation was then used to compute $P°_L$ of test compounds from their measured $P°_{GC}$. $P°_L$ of seven major components of technical chlordane, endosulfan and its metabolites, α-hexachlorocyclohexane, mirex, and two components of technical toxaphene were determined by GC. This method provides vapor pressures within a factor of 2 of average literature values for nonpolar compounds, similar to reported interlaboratory precisions of vapor pressure determinations. GC tends to overestimate vapor pressures of moderately polar compounds.

Introduction

The vapor pressure of an organic chemical exerts a large influence on its dispersal in the environment and must be considered when the environmental fate of the substance is modeled (*1–4*). In a previous article (*5*), we discussed two conventional methods for determining vapor pressures of low-volatility chemicals (gas saturation and effusion) and offered capillary gas chromatography (GC) as an alternative technique for use with nonpolar compounds. The advantages of GC are that several compounds can be run per day and only very small quantities of the chemical are required. This latter feature is an important consideration when dealing with highly toxic or costly compounds. An example of the GC method for such applications is the determination of vapor pressures for polychlorinated dibenzo-p-dioxins (*6*).

In previous articles (*5*, *7*), the correlation between the relative retention volume (or time), $V_{R,1}/V_{R,2}$, of two compounds was expressed by

$$\ln (V_{R,1}/V_{R,2}) = [1 - (\Delta H_{L,1}/\Delta H_{L,2})] \ln P°_{L,2} - C \quad (1)$$

where 1 and 2 refer to the test and reference compounds, $P°_{L,2}$ is the liquid-phase saturation vapor pressure of the reference compound at a particular temperature, $\Delta H_{L,1}$ and $\Delta H_{L,2}$ are the enthalpies of vaporization of the solutes, and C is a constant. This equation is an approximation, since (*8*)

$$V_{R,1}/V_{R,2} = \gamma_2 P°_{L,2}/\gamma_1 P°_{L,1} \quad (2)$$

In eq 2, γ_1 and γ_2 are the infinite dilution activity coefficients of the solutes in the stationary phase. The correct correlation equation is therefore

$$\ln (V_{R,1}/V_{R,2}) = [1 - (\Delta H_{L,1}/\Delta H_{L,2})] \ln P°_{L,2} - \ln \gamma_1/\gamma_2 - C \quad (3)$$

which arises from combination of eq 2 with eq 4 below. The success of the GC method hinges on the assumption that $\gamma_1 = \gamma_2$.

The experimental and computational procedures for determining vapor pressures from GC data were given in a previous article (*5*). Briefly, the steps are as follows:

(1) Test compounds and a reference compound of known vapor pressure are cochromatographed on a 1.0-m capillary column coated with a nonpolar stationary phase. Several isothermal runs are made, typically in the 70–150 °C range. Values of ln ($V_{R,1}/V_{R,2}$) are plotted vs ln ($P°_{L,2}$) at each temperature. $\Delta H_{L,1}/\Delta H_{L,2}$ and the constant C are evaluated from the slope and intercept of eq 1.

(2) An estimate of the test compound's vapor pressure, $P°_{L,1}$, at ambient temperature is made from the enthalpy ratio and the vapor pressure of the reference compound at the same temperature:

$$\ln P°_{L,1} = (\Delta H_{L,1}/\Delta H_{L,2}) \ln P°_{L,2} + C \quad (4)$$

Hereafter, we refer to this vapor pressure estimate as $P°_{GC}$ (*5*). When the GC method was applied to a series of organochlorines and aromatic hydrocarbons having known $P°_L$ (standard compounds), we found the $P°_{GC}$ was well correlated with but in most cases not equal to the standard compound's $P°_L$. This discrepancy probably arises because of activity coefficient differences between the reference and standard compounds; that is, $\gamma_1 \neq \gamma_2$. An attempt to correct for this effect was made by preparing a calibration plot of log $P°_{GC}$ vs log $P°_L$ for the standard compounds, which then allowed $P°_L$ of unknown compounds to be determined from their measured $P°_{GC}$ values.

The accuracy of this method depends to a large extent on (a) the accuracy of the $P°_L$ values for the GC reference compound and the standard compounds used to establish the log $P°_{GC}$ vs log $P°_L$ regression and (b) the similarity in activity coefficients among reference, standard, and unknown test compounds. Literature vapor pressures of low-volatility sub-

---

[†] Marine Science Program, University of South Carolina.

[‡] Current address: Ebasco Environmental, 10900 N.E. 8th St., Bellevue, WA 98004.

[§] Department of Chemistry, University of South Carolina.

[⊥] Belle W. Baruch Institute for Marine Biology and Coastal Research, University of South Carolina.

[∥] Current address: Methods Research and Development Program, National Water Quality Laboratory, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002.

[#] Current address: Weston Analytical, 208 Welsh Pool Rd., Lyonville, PA 19353.

0021-9568/90/1735-0232$02.50/0 © 1990 American Chemical Society

stances often disagree by a factor of 2-3 or more (*5*). Also, many high molecular weight organic compounds are solids at ambient temperatures, and reported vapor pressures are usually those of the crystalline solid, P°_S. Interconversion of P°_L and P°_S can be done with

$$\ln P^\circ_L/P^\circ_S = (\Delta S_f/R)(T_m - T)/T \qquad (5)$$

In eq 5, T_m and T are the melting and ambient temperatures (kelvin), R is the gas constant, and ΔS_f is the entropy of fusion. Average values of ΔS_f are 56.5 J/deg-mol for rigid aromatic hydrocarbons (*9*) and 54.9 J/deg-mol for polychlorinated biphenyl (PCB) congeners (*10*), but substantial differences occur among compounds. For example, the range of ΔS_f for several PCB congeners is 41.9-71.2 J/deg-mol (*11*).

In this study we have made several changes to improve the GC vapor pressure technique. Two important changes were as follows:

(1) Values of ΔS_f were obtained from the literature, or in some cases experimentally determined by us, for many of the standard compounds. These "actual" ΔS_f values were used to convert literature P°_S to P°_L, instead of the "average" ΔS_f = 56.5 J/deg-mol ($\Delta S_f/R$ = 6.79) previously assumed (*5*).

(2) A new GC reference compound, *p,p'*-DDT, was selected to supplement the *n*-alkane references eicosane and octadecane previously used (*5*). The P°_S and ΔS_f of *p,p'*-DDT have been well established by several investigators (refs 11-16 and this work). Moreover, *p,p'*-DDT is electron capture detector (ECD) responsive whereas a flame ionization detector (FID) is required for the *n*-alkanes. Use of an ECD is advantageous in that small quantities of halogenated test compounds can be chromatographed, reducing the possibility of overloading the short capillary column used in this method (*5*).

We have used these modifications to determine P°_L of several organochlorine insecticides including endosulfan and its metabolites, major constituents of technical chlordane, and two toxic components of technical toxaphene. From the change $V_{R,1}/V_{R,2}$ with temperature, Clausius-Clapeyron equations have been developed that allow calculation of P°_L at different temperatures. The limitations of the GC method when applied to somewhat polar molecules such as phthalate esters and organophosphate and pyrethroid insecticides have been examined.

Experimental Section

Hydrocarbon and pesticide standards of ≥99% purity were obtained from Analabs, Inc., and the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository, Research Triangle Park, NC, respectively. Endosulfan lactone and endosulfan ether (≥99% purity) were purchased from Crescent Chemical Co. Analytical standards of toxicants A and B, components of technical toxaphene, were supplied by Dr. Jay Gooch, Woods Hole Oceanographic Institution, and the Special Analytical Laboratory, National Environmental Protection Board, Sweden. Pesticide standards were used as received. Solvents were J. T. Baker Resi-Analyzed.

Test and reference compounds were chromatographed on a poly(dimethylsiloxane) bonded-phase fused silica column (BP-1, SGE Inc.) 1.0-m length × 0.22-mm i.d., film thickness 0.33 μm, mounted in a Carlo Erba Model 4160 or Varian Model 3700 instrument. A series of four to seven isothermal runs in the 70-180 °C range was made for each compound as previously described (*5*) with use of either an ECD or FID. Conditions: carrier gas H_2 or He at 1-3 mL/min, injector 150-240 °C, detector 300-320 °C. Samples in *n*-hexane were injected at a 10:1 or 20:1 split ratio. The data treatment was as described in ref 5.

Table I. Entropy of Fusion (ΔS_f, J/deg-mol) for Standard Compounds

compound	lit. value (ref)	selected value
naphthalene	52.7 (*20*)	52.7
biphenyl	49.4 (*20*), 51.1 (*9*), 58.2 (*11*), 54.0 (*17*), 54.4 (*11*), 49.0 (*11*), 55.3 (*11*)	53.6
fluorene	51.1 (*20*)	51.1
hexachlorobenzene	44.4 (*11*), 47.3 (*20*)	46.1
phenanthrene	47.7 (*18*), 49.8 (*20*)	48.6
anthracene	55.7 (*18*), 60.3 (*20*)	57.8
aldrin	46.5 (*19*)	46.5
γ-HCH	41.4 (*11*), 61.1 (this work)	61.1
pyrene	54.8 (*20*)	54.8
dieldrin	41.0 (*19*), 47.7 (*19*)	44.4
2,2',5,5'-tetrachlorobiphenyl	46.1 (this work)	46.1
fluoranthene	47.7 (this work)	47.7
p,p'-DDE	67.0 (*11*)	67.0
2,2',4,5,5'-pentachlorobiphenyl	53.6 (*10*)	53.6
o,p'-DDT	69.9 (*12*), 70.3 (this work), 78.3 (*11*)	72.8
p,p'-DDD	81.2 (*11*)	81.2
2,2',3,3',5,5',6,6'-octachlorobiphenyl	52.7 (*10*)	52.7
p,p'-DDT	69.1 (*11*), 71.2 (this work), 74.5 (*12*)	71.6
decachlorobiphenyl	49.4 (this work)	49.4
benzo[*e*]pyrene	42.3 (this work)	42.3
benzo[*a*]pyrene	38.5 (this work)	38.5

Differential scanning calorimetry (DSC) was used to establish ΔS_f for the compounds reported here. The analysis involved accurately weighing a sample (1-3 mg) of neat material into an aluminum pan, which was then heated at a rate of 1.25 deg/min. Instrumentation was a Perkin-Elmer Model DSC-2C with a 3600 data station and purity analysis software. High-purity indium was used to calibrate temperature and the ΔH_f calculation. Samples of phenacetin doped with varying levels of *p*-aminobenzoic acid (NBS SRM 1514) were analyzed as quality control reference materials to assure proper performance throughout the analysis and data reduction steps.

The resulting DSC melting data were evaluated with vendor-provided (PE) software, which is based on the van't Hoff equation (*11*). Briefly, the program plots $1/F$ versus temperature where F is the fraction melted at the corresponding temperature. The intercept provided T_m (the melting point of pure material), and the area under the melting peak produced ΔH_f (J/mol). For each compound, ΔS_f was calculated according to the equation

$$\Delta S_f = \Delta H_f/T_m \qquad (6)$$

Assumptions pertinent to this DSC procedure are that the compound is high purity (>95%), melts in an ideal manner, and has a ΔS_f greater than 21 J/deg-mol.

Results and Discussion

In our original study (*5*), compounds were chromatographed on a bonded-phase (BP-1) column and a WCOT column containing *n*-C_{87} (Apolane-87). The Apolane-87 column has since been discontinued by its only manufacturer, consequently only the BP-1 column was used in the present investigation. The carrier gas was switched from He to H_2 midway through the project, and improved column efficiency was observed.

Entropies of fusion for many of the standard and GC reference compounds were obtained from the literature (*10-12*, *17-20*) or were determined by using DSC. These ΔS_f and the values selected for conversion of P°_S to P°_L are given in Table I.

Vapor Pressure of the GC Reference Compound p,p'-DDT. Over short temperature ranges where the enthalpy of sublimation or vaporization is approximately constant, the vapor

Table II. Coefficients for Equations 7 and 8 for *p,p'*-DDT (Pa)

	$P°_S$		$P°_L$		
	A_S	B_S	A_L	B_L	ref
	16.37	-6176	12.80	-4802	13
	15.91	-6010	12.20	-4589	14
	15.40	-5851	11.68	-4424	15
	16.32	-6160	12.63	-4747	16
$\bar{X}$	16.00	-6049	12.33	-4640	

Table III. Vapor Pressures of Standard Compounds at 25 °C

compound	log [$P°_{GC}$ (Pa)]		log [$P°_L$ (Pa)][a]	
	C_{20}	*p,p'*-DDT	1	2
naphthalene	1.355		1.622	1.580
1-methylnaphthalene	0.871		0.946[b]	
1,2,3,4-tetrachlorobenzene	0.604		0.903	
biphenyl	0.525		0.749	0.699
2-chlorobiphenyl	0.040		0.265[b]	
4-chlorobiphenyl	-0.228		0.150[b]	
fluorene	-0.325		-0.101	-0.186
hexachlorobenzene	-0.799	-0.923	-0.518	-0.896
phenanthrene	-0.954	-1.255	-0.874	-1.000
anthracene	-0.998	-1.162	-1.063	-1.028
aldrin	-1.636	-1.694	-0.979	-1.121
γ-HCH	-0.970	-1.151	-1.258	-1.188
2,4,6-trichlorobiphenyl	-1.063		-1.523[b]	
pyrene	-1.946	-2.124	-1.801	-1.842
dieldrin	-2.274	-2.498	-1.667	-1.994
2,2',5,5'-tetrachlorobiphenyl	-1.726	-1.921	-1.983	-2.097
fluoranthene	-1.811	-2.020	-2.065	-2.197
p,p'-DDE	-2.568	-2.729	-2.594	-2.476
2,2',4,5,5'-pentachlorobiphenyl	-2.298	-2.469	-2.502	-2.529
C_{20}		-2.757	-2.581[b]	
o,p'-DDT	-2.792	-2.985	-2.877	-2.738
p,p'-DDD	-2.789	-2.958	-3.362	-3.007
benz[*a*]anthracene	-2.969	-3.491	-3.265	
2,2',3,3',5,5',6,6'-octachlorobiphenyl		-3.654	-3.181	-3.279
p,p'-DDT	-3.081		-3.500	-3.291
decachlorobiphenyl		-4.885	-5.289	-4.842
benzo[*e*]pyrene		-4.066	-4.597	-4.991
benzo[*a*]pyrene	-3.951	-4.140	-4.629	-5.138

[a] References as cited in ref 5 with the addition of ref 25. Conditions: (1) using $\Delta S_f/R = 6.79$. (2) using actual $\Delta S_f/R$ (Table I). [b] $P°_L$ obtained from literature, no conversion from $P°_S$ required.

Table IV. Regression Parameters for log $P°_L$ = m log $P°_{GC}$ + b (equation 10)

vapor press ref	$P°_S$-to-$P°_L$ conversion	m	b	r^2	stand. error of regressn
n-C_{20}, $n = 24$	*a*	1.140	0.179	0.967	0.303
n-C_{20}, $n = 24$	*b*	1.142	0.139	0.967	0.300
p,p'-DDT, $n = 19$	*a*	1.168	0.522	0.939	0.343
p,p'-DDT, $n = 19$	*b*	1.135	0.382	0.920	0.384

[a] ΔS_f = 56.5 J/deg-mol. [b] Actual ΔS_f from Table I were used for all compounds except those for which ΔS_f are not available. In these cases, the default $\Delta S_f/R = 6.79$ was used.

Table V. Comparison of Vapor Pressures of Pesticides Using Different Reference Standards

compound	$P°_L$ at 25 °C, Pa	
	n-C_{20} ref	*p,p'*-DDT ref
α-HCH	0.227	0.227
mirex	2.5×10^{-4}	2.9×10^{-4}
endosulfan I	5.9×10^{-3}	6.4×10^{-3}
endosulfan II	2.5×10^{-3}	3.7×10^{-3}
endosulfan sulfate	1.1×10^{-3}	1.5×10^{-3}
trans-chlordane	6.3×10^{-3}	6.9×10^{-3}
cis-chlordane	4.5×10^{-3}	5.1×10^{-3}
cypermethrin	2.0×10^{-6}	2.4×10^{-6}
fenvalerate	8.8×10^{-7}	8.4×10^{-7}

pressure is related to temperature by the Clausius–Clapeyron equations:

$$\log P°_S = A_S + B_S/T \tag{7}$$

$$\log P°_L = A_L + B_L/T \tag{8}$$

$B_S = -\Delta H_S/2.303R$ and $B_L = -\Delta H_L/2.303R$ where ΔH_S and ΔH_L are the enthalpies of sublimation and vaporization, respectively. The $P°_S$ of *p,p'*-DDT as a function of temperature has been determined by gas saturation (*13–16*), and the coefficients A_S and B_S reported by four laboratories are given in Table II. Conversions from $P°_S$ to $P°_L$ were made (eq 5) using ΔS_f = 71.6 J/deg-mol (Table I) and T_m = 392, and coefficients A_L and B_L were calculated for eq 8 (Table II). Average A_L and B_L values were used to produce the working relationship

$$\log P°_L(\text{Pa, } p,p'\text{-DDT}) = 12.33 - 4640/T \tag{9}$$

from which log $P°_L$ at various temperatures was calculated.

Vapor Pressures of Standard Compounds. Nineteen hydrocarbon and organochlorine standard compounds with known $P°_L$ were chromatographed along with the *p,p'*-DDT reference, and $P°_{GC}$ at 25 °C were calculated from the relative retention data as previously described (*5*). In Table III, these $P°_{GC}$ are compared to $P°_L$ obtained from eq 5 with actual ΔS_f (Table I) and an assumed ΔS_f (default value) of 56.5 J/deg-mol. Also shown are $P°_{GC}$ values of 24 standard compounds previously determined with use of the C_{20} reference (*5*).

In previous work (*5*), two factors were identified that caused $P°_{GC}$ determined on a BP-1 column to be unequal to $P°_L$. One was a systematic error, attributed to the column, in which $P°_{GC}$ underestimated and overestimated $P°_L$ at the high- and low-volatility ends of the scale. This might occur if the differences in γ among the standard compounds were related to compound volatility. An attempt was made to correct for this bias by using a regression relationship between log $P°_{GC}$ and log $P°_L$, with the hope that the variations in γ with volatility for unknown test compounds were similar to those of the standards. In addition to this bias, a scatter of points about the regression line was observed. These deviations for individual compounds could be due to differences in γ, which were not correlated with volatility, to uncertainties in literature values for their vapor pressures, and to inaccuracies in computing $P°_L$ from reported $P°_S$. We thought the latter situation might be improved by using actual rather than default ΔS_f values. A compound-by-compound comparison (Table III) shows that use of actual ΔS_f improved the agreement between $P°_{GC}$ and $P°_L$ in some cases (notably hexachlorobenzene, dieldrin, *p,p'*-DDD, *p,p'*-DDT, and decachlorobiphenyl) but made it worse for the benzopyrenes.

Linear regression analysis was done to fit

$$\log P°_L = m \log P°_{GC} + b \tag{10}$$

using $P°_{GC}$ values obtained with either the *p,p'*-DDT or C_{20} reference and $P°_L$ values calculated from eq 5 with both actual and default ΔS_f. Slopes and intercepts for eq 10 for each analysis are shown in Table IV. Figure 1 is the regression plot of log $P°_L$ vs log $P°_{GC}$ for the *p,p'*-DDT reference with use of actual ΔS_f. Also shown is the 95% confidence interval for the mean predicted log $P°_L$. No significant differences in slopes and intercepts were found between actual and default ΔS_f for either reference standard (F-test, $\alpha > 0.75$). It thus appears that the main cause of scatter about the regression is uncertainties in literature values for the vapor pressures of the standards or variations in their γ values. Nevertheless, the improved agreement between $P°_{GC}$ and $P°_L$ with actual ΔS_f values for a number of compounds indicates that such information should be used if available.

Application to Compounds of Unknown Vapor Pressures. Vapor pressures of several nonpolar and polar compounds

Table VI. Vapor Pressures of Test Compounds, P°_L, Pa (25 °C)

compound	standard[a]	P°_L GC method	P°_L lit.	ref	accuracy ref ratio[b]
Chlordane Components					
heptachlor	A	3.1×10^{-2}			
α-chlordene	A	2.4×10^{-2}			
γ-chlordene	A	1.6×10^{-2}			
trans-chlordane	A,B	6.7×10^{-3}			
cis-chlordane	A,B	4.8×10^{-3}			
trans-nonachlor	A,B	3.7×10^{-3}			
cis-nonachlor	A	1.6×10^{-3}			
Endosulfan and Metabolites					
endosulfan ether	B	6.5×10^{-2}			
endosulfan lactone	B	9.6×10^{-3}			
endosulfan I	A,B	6.1×10^{-3}	1.3×10^{-2}	22	0.5
endosulfan II	A,B	3.2×10^{-3}			
endosulfan sulfate	A,B	1.3×10^{-3}			
Other Organochlorine Compounds					
α-HCH	A,B	2.3×10^{-1}	2.7×10^{-1}[d]	16	0.9
mirex	A,B	2.8×10^{-4}			
toxicant B[c]	A	2.1×10^{-3}			
toxicant A[c]	B	1.1×10^{-3}			
Organophosphate Pesticides and Flame Retardents					
phorate	A	1.1×10^{-1}	7.3×10^{-2}	26	1.5
			2.5×10^{-1}	27	0.4
diazinon	A	2.0×10^{-2}	1.1×10^{-2}	26	1.8
			2.0×10^{-2}[d]	28	1.0
methyl parathion	A	2.3×10^{-2}	2.0×10^{-3}	26	11.3
			2.3×10^{-3}	29	10.0
ethyl parathion	A	6.7×10^{-3}	1.2×10^{-3}	26	5.4
			1.3×10^{-3}	29	5.2
			8.0×10^{-3}[d]	29	0.8
			4.7×10^{-3}	29	1.4
malathion	A	4.7×10^{-3}	1.1×10^{-3}	26	4.4
			2.9×10^{-3}	27	1.6
fenitrothion	A	1.1×10^{-2}	5.5×10^{-3}	30	2.0
chlorpyrifos	A	6.7×10^{-3}	3.9×10^{-3}	26	1.7
			3.7×10^{-3}	31	1.8
tris(butoxyethyl) phosphate	A	2.8×10^{-5}	2.4×10^{-5}[d]	32	1.2
tris(2-ethylhexyl) phosphate	A	1.1×10^{-5}	2.9×10^{-5}	32	0.4
tricresyl phosphate	A	6.1×10^{-6}	2.9×10^{-6}[d]	32	2.1
Phthalates					
dimethyl phthalate	A	1.19	0.240	32	4.9
			0.227	33	5.2
diethyl phthalate	A	2.8×10^{-1}	8.5×10^{-2}	32	3.3
			2.3×10^{-1}[d]	33	1.2
			8.1×10^{-2}	34	3.4
di-*n*-butyl phthalate	A	5.6×10^{-3}	2.7×10^{-3}	32	0.5
			9.7×10^{-3}	33	0.6
			5.9×10^{-3}[d]	35	1.0
			4.1×10^{-3}[d]	36	1.4
			7.6×10^{-5}	39	74
bis(2-ethylhexyl) phthalate	A	1.9×10^{-5}	1.9×10^{-5}[d]	32	1.0
			8.7×10^{-4}	33	0.02
			2.4×10^{-5}[d]	36	0.8
			1.2×10^{-5}[d]	36	1.5
			8.3×10^{-6}	39	2.3
Synthetic Pyrethroids					
cis-permethrin	B	1.0×10^{-5}	4.8×10^{-6}[d]	22	2.1
			4.9×10^{-6}[d]	37	2.0
trans-permethrin	B	8.1×10^{-6}	3.7×10^{-6}[d]	22	2.2
			3.1×10^{-6}[d]	37	2.7
cypermethrin	A,B	2.4×10^{-6}	8.7×10^{-7}[d]	22	2.8
			4.3×10^{-7}	38	5.6
fenvalerate	A,B	8.1×10^{-7}	4.9×10^{-7}[d]	22	1.6

[a] A = C_{20}, B = *p,p'*-DDT. [b] Accuracy ratio = this work/literature. [c] Components of technical toxaphene, toxicant B = 2,2,5-*endo*-6-*exo*-8,9,10-heptachlorobornane; toxicant A = two unresolved octachlorobornanes (*21*). [d] Agreement with GC method within 95% confidence interval, see Figure 1.

were determined by GC. The compound classes were organochlorine, organophosphate, and pyrethroid insecticides, organophosphate flame retardants, and phthalate esters. These substances were chromatographed along with *p,p'*-DDT and/or eicosane references. Values of P°_L were calculated from measured P°_{GC} with eq 10 and the regression parameters in Table IV (actual ΔS_f values). In cases where both C_{20} and *p,p'*-DDT references were used, the resulting P°_L values

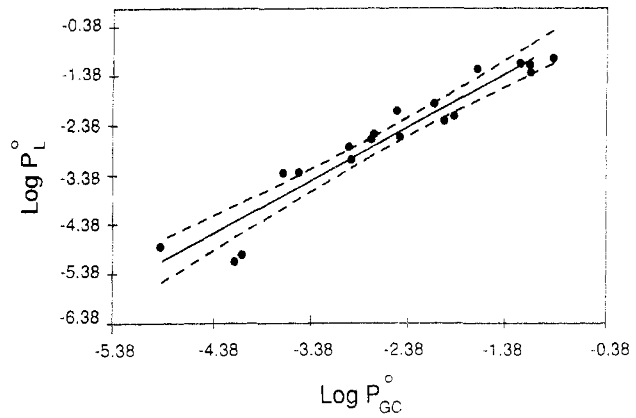

Figure 1. Comparison of literature liquid-phase vapor pressures (P°_L) by using actual ΔS_f with P°_{GC} for the *p,p'*-DDT reference standard. Dotted lines represent the 95% confidence interval for the mean predicted P°_L.

Table VII. Parameters for log [P°_L (Pa)] = A_L + B_L/T

	lit. data[a]		this work	
compound	B_L	A_L	B_L	A_L
anthracene	-3534	10.83	-3642	11.18
phenanthrene	-3802	11.77	-3716	11.46
fluoranthene	-3480	9.48	-4040	11.35
pyrene	-3761	10.62	-4104	11.92
benz[*a*]anthracene	-4208	10.84	-4742	12.63
benzo[*a*]pyrene	-5282	12.63	-4989	11.59
benzo[*e*]pyrene	-5238	12.57	-4803	11.11
tetrachlorobiphenyl	-4032	11.42	-4127	11.74
pentachlorobiphenyl	-3882	10.49	-4369	12.13
octachlorobiphenyl	-4119	10.53	-4851	12.99
decachlorobiphenyl	-4879	11.52	-5402	13.27
α-HCH	-3301	10.49	-3575	11.34
γ-HCH	-4416	13.63	-3680	11.15
p,p'-DDT	-4640	12.32	-4865	13.02
o,p'-DDT			-4626	12.77
p,p'-DDD			-4622	12.49
p,p'-DDE			-4554	12.79
aldrin	-3773	11.53	-3924	12.04
dieldrin	-3965	11.30	-4310	12.46
cis-chlordane			-4284	12.04
trans-chlordane			-4216	11.96
trans-nonachlor			-4468	12.56
cis-nonachlor			-4378	11.88
heptachlor			-3995	11.88
hexachlorobenzene	-3561	11.04	-3582	11.11
toxicant A			-4394	11.77
toxicant B			-4579	12.68
mirex			-4718	12.27
endosulfan ether			-3704	11.23
endosulfan lactone			-4077	11.65
endosulfan I			-4201	11.87
endosulfan II			-4306	12.08
endosulfan sulfate			-4470	12.11

[a] Equation 5 was used to convert P°_S to P°_L.

showed excellent agreement (Table V).

Vapor pressures (P°_L) of all test compounds at 25 °C are given in Table VI. For compounds where P°_L was determined with both C_{20} and *p,p'*-DDT references, the average P°_L is reported. Only two of the organochlorine pesticides had literature data available for comparison. Balson (*16*) determined P°_L of α-HCH using effusion. Barlow (*22*) reported relative volatilization rates for endosulfan I and *p,p'*-DDT, from which P°_S of endosulfan I was estimated by a procedure similar to that applied by Dobbs and Grant (*23*). The agreement between literature P°_L and P°_L determined by GC was reasonably good for these two pesticides (Table VI). The determination of P°_L for toxicants A and B illustrates an important application of the GC method. These toxic components of technical toxaphene (*21*) are not available commercially and could only be obtained in microgram quantities from laboratories involved in toxaphene research. Their vapor pressures probably could not have been determined in any other way.

Vapor pressures of PCB congeners presented earlier (*5*) were recalculated with the C_{20} regression based on actual ΔS_f values (Table IV). The resulting P°_L differed inconsequentially from those originally reported. We compared our P°_L of PCBs to values recently determined by a static equilibrium method (*24*). The average accuracy ratio (AR) of GC method to literature method (in this case, static equilibrium) was 1.5 ± 0.7 (n = 16). These comparisons, along with those for α-HCH and endosulfan I attest to the accuracy of the GC method for determining P°_L of nonpolar compounds.

Clausius–Clapeyron (eq 8) coefficients A_L and B_L for several PAH and organochlorines, calculated from literature and experimental GC data, are given in Table VII. Insertion of the appropriate A_L and B_L into eq 8 allows prediction of P°_L at different temperatures.

The performance of the GC method with moderately polar compounds was tested with organophosphate and pyrethroid insecticides, phthalates, and organophosphate flame retardants (Table VI). The AR values for phthalates decrease as the aliphatic chain length increases, indicating that longer carbon chain lengths may increase the nonpolar nature of the molecule, and bring its γ closer to those of the reference and standard compounds. The same trend is observed when the organophosphates are compared: flame retardants with large, bulky organic groups had a lower AR than the smaller organophosphate insecticides. P°_L values for organophosphate pesticides showed an average AR of 3.4, with a wide range from 0.4 to 11.3. It is important to note that this AR can vary a great deal for the same compound. The AR for ethyl parathion ranges from 5.4 to 0.8, depending on which literature value is used for comparison. Again, the problem of variability in literature vapor pressures is readily apparent. The average AR for synthetic pyrethroids was 2.9, although elimination of one high literature value for cypermethrin decreased the average AR to 2.4 (Table VI).

In general, the GC method overestimated P°_L of polar compounds when P°_L was calculated from P°_{GC} by using eq 10 and the parameters for the nonpolar calibration curve (Table IV). Early elution of polar compounds (relative to nonpolar solutes of the same P°_L) on a nonpolar stationary phase can be accounted for by eq 2, where $\gamma_2 > \gamma_1$. A large body of literature exists in which infinite dilution activity coefficients have been determined by GC. A paper by Nitta et al. (*40*) exemplifies the situation for solutes on the nonpolar stationary-phase squalane. Values of γ ranged from 0.48 to 0.73 for aliphatic and aromatic hydrocarbons, from 2.0 to 3.7 for ketones and esters, and from 17 to 39 for alcohols and acetonitrile. Clearly differences in γ between a nonpolar reference compound and a polar test compound can lead to a large error in estimating the latter's vapor pressure.

An alternative approach to determining vapor pressures for polar solutes is to use a polar reference compound of the same chemical class. For example, Kim et al. (*26*) used ethyl parathion as a reference to determine P°_{GC} of other organophosphate pesticides. However, the variation in γ among polar solutes is likely to be considerably greater than among nonpolar ones, making the accuracy of this procedure problematic.

Summary

Gas chromatography is a quick and easy way to determine P°_L of a compound. On the basis of the 95% CI for eq 10 (Table VI), P°_L for nonpolar hydrocarbons and organochlorines can be determined within a factor of 2 of literature values, well within the interlaboratory precision of other techniques. The accuracy of the GC method depends not only on test compound literature values but on the assumption that the infinite dilution activity coefficient (γ) of the reference and test compound is equal. The latter assumption can lead to problems when GC is used to determine P°_L for polar substances. P°_{GC} overestimates P°_L by up to factors of 5-10 for some organophosphate pesticides and phthalate esters. Caution should be exercised when applying the GC method to these and other polar substances.

Acknowledgment

Portions of this work were performed while T.F.B. was on sabbatical leave at the National Environmental Protection Board, Sweden. We thank Jay Gooch of Woods Hole Oceanographic Institution for his gift of toxicant A.

Registry No. γ-HCH, 58-89-9; *p*,*p*′-DDE, 72-55-9; *o*,*p*′-DDT, 789-02-6; *p*,*p*′-DDD, 72-54-8; *p*,*p*′-DDT, 50-29-3; α-HCH, 319-84-6; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 1,2,3,4-tetrachlorobenzene, 634-66-2; biphenyl, 92-52-4; 2-chlorobiphenyl, 2051-60-7; 4-chlorobiphenyl, 2051-62-9; fluorene, 86-73-7; hexachlorobenzene, 118-74-1; phenanthrene, 85-01-8; anthracene, 120-12-7; aldrin, 309-00-2; 2,4,6-trichlorobiphenyl, 35693-92-6; pyrene, 129-00-0; dieldrin, 60-57-1; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; fluoranthene, 206-44-0; 2,2′,4,5,5′-pentachlorobiphenyl, 37680-73-2; eicosane, 112-95-8; benz[*a*]anthracene, 56-55-3; 2,2′,3,3′,5,5′,6,6′-octachlorobiphenyl, 2136-99-4; decachlorobiphenyl, 2051-24-3; benzo[*e*]pyrene, 192-97-2; benzo[*a*]pyrene, 50-32-8; mirex, 2385-85-5; endosulfan I, 959-98-8; endosulfan II, 33213-65-9; endosulfan sulfate, 1031-07-8; *trans*-chlordane, 5103-74-2; *cis*-chlordane, 5103-71-9; cypermethrin, 52315-07-8; fenvalerate, 51630-58-1; heptachlor, 76-44-8; α-chlordene, 56534-02-2; γ-chlordene, 56641-38-4; *trans*-nonachlor, 39765-80-5; *cis*-nonachlor, 5103-73-1; endosulfan ether, 3369-52-6; endosulfan lactone, 3868-61-9; phorate, 298-02-2; diazinon, 333-41-5; methyl parathion, 298-00-0; ethyl parathion, 56-38-2; malathion, 121-75-5; fenitrothion, 122-14-5; chlorpyrifos, 2921-88-2; tris(butoxyethyl) phosphate, 78-51-3; tris(2-ethylhexyl) phosphate, 78-42-2; tricresyl phosphate, 1330-78-5; dimethyl phthalate, 131-11-3; diethyl phthalate, 84-66-2; di-*n*-butyl phthalate, 84-74-2; bis(2-ethylhexyl) phthalate, 117-81-7; *cis*-permethrin, 61949-76-6; *trans*-permethrin, 61949-77-7.

Literature Cited

(1) Mackay, D.; Paterson, S. *Environ. Sci. Technol.* **1982**, *16*, 654A-660A.
(2) Valsaraj, K. T.; Thibodeaux, L. J. *J. Hazard. Mater.* **1988**, *19*, 79-99.
(3) Bidleman, T. F. *Environ. Sci. Technol.* **1988**, *22*, 361-367.
(4) Jury, W. A.; Spencer, W. F.; Farmer, W. J. *J. Environ. Qual.* **1984**, *13*, 567-586.
(5) Bidleman, T. F. *Anal. Chem.* **1984**, *56*, 2490-2496.
(6) Eitzer, B. D.; Hites, R. A. *Environ. Sci. Technol.* **1988**, *22*, 1362-1364.
(7) Hamilton, D. J. *J. Chromatogr.* **1980**, *195*, 75-83.
(8) Martire, D. E.; Pollara, L. Z. In *Advances in Chromatography*; Giddings, J. C., Keller, R. A., Eds.; Marcel Dekker Inc.: New York, 1965; Vol. 1, No.10, pp 335-362.
(9) Yalkowski, S. H. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 108-111.
(10) Miller, M. M.; Ghodbane, S.; Wasik, S. P.; Tewari, Y. B.; Martire, D. E. *J. Chem. Eng. Data* **1984**, *29*, 184-190.
(11) Plato, C.; Glasgow, A. R., Jr. *Anal. Chem.* **1969**, *41*, 330-336.
(12) Haller, H. L.; Bartlett, P. D.; Drake, N. L.; Newman, M. S.; Cristol, S. J.; Eaker, C. M.; Hayes, R. A.; Kilmer, G. W.; Barney, M.; Muller, G. P.; Schneider, A.; Wheatley, W. *J. Am. Chem. Soc.* **1945**, *67*, 1591-1602.
(13) Spencer, W. F.; Cliath, M. M. *J. Agric. Food Chem.* **1972**, *20*, 645-649.
(14) Dickinson, W. *Trans. Faraday Soc.* **1956**, *52*, 31-35.
(15) Rothman, A. M. *J. Agric. Food Chem.* **1980**, *28*, 1225-1229.
(16) Balson, E. W. *Trans. Faraday Soc.* **1947**, *43*, 54-60.
(17) Parks, G. S.; Huffman, H. M. *Ind. Eng. Chem.* **1931**, *23*, 1138-1139.
(18) Dekruif, C. G. *J. Chem. Thermodyn.* **1980**, *12*, 243-248.
(19) Plato, C. *Anal. Chem.* **1972**, *44*, 1531-1534.
(20) Mackay, D.; Shiu, W. Y. *J. Chem. Eng. Data* **1977**, *22*, 399-402.
(21) Khalifa, A.; Mon, T. R.; Engel, J. L.; Casida, J. E. *J. Agric. Food Chem.* **1974**, *22*, 653-657.
(22) Barlow, F. Presented at the 4th International Congress of Pesticide Chemistry, Zurich, Switzerland, July 24-28, 1978.
(23) Dobbs, A. J.; Grant, C. *Pestic. Sci.* **1980**, *11*, 29-32.
(24) Murphy, T. J.; Mullin, M. D.; Meyer, J. A. *Environ. Sci. Technol.* **1987**, *21*, 155-162.
(25) Burkhard, L. P.; Armstrong, D. E.; Andren, A. W. *J. Chem. Eng. Data* **1984**, *29*, 248-250.
(26) Kim, Y.; Woodrow, J. E.; Seiber, J. N. *J. Chromatogr.* **1984**, *314*, 37-53.
(27) Woolford, M. H., Jr. American Cyanamid Co., letter to W. F. Spencer, September 3, 1975.
(28) Marti, E. Ciba-Geigy Ag, letter to W. F. Spencer, April 23, 1976.
(29) Spencer, W. F.; Shoup, T. D.; Cliath, M. M.; Farmer, W. J.; Haque, R. *J. Agric. Food Chem.* **1979**, *27*, 273-278.
(30) Addison, J. B. *Chemosphere* **1981**, *10*, 355-364.
(31) Hamaker, J. W. Dow Chemical Co., letter to W. F. Spencer, July 21, 1975.
(32) Small, P. A.; Small, K. W.; Cowley, P. *Trans. Faraday Soc.* **1948**, *44*, 810-816.
(33) Howard, P. H.; Banerjee, S.; Robillard, K. H. *Environ. Toxicol. Chem.* **1985**, *4*, 653-661.
(34) Grayson, B. T.; Fosbraey, L. A. *Pestic. Sci.* **1982**, *13*, 269-278.
(35) Perry, E. S.; Weber, W. H. *J. Am. Chem. Soc.* **1949**, *71*, 3726-3730.
(36) Results of Interlaboratory Calibration Study. Final Report; OECD Chemicals Testing Programme, Expert Group on Physical Chemistry: Berlin, Dec 1979; Table 4.17, p 41.
(37) Wells, D.; Grayson, B. T.; Langner, E. *Pestic. Sci.* **1986**, *17*, 473-476.
(38) Grayson, B. T.; Langner, E.; Wells, D. *Pestic. Sci.* **1982**, *13*, 552-556.
(39) Werner, A. C. *Ind. Eng. Chem.* **1952**, *44*, 2736-2740.
(40) Nitta, T.; Morinaga, K.; Katayama, T. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 396-401.

Received for review June 9, 1989. Accepted February 21, 1990. This work was supported by the South Carolina Sea Grant Consortium. Portions of this work were presented at the Society of Environmental Toxicology and Cemistry Seventh Annual Meeting, Alexandria, Virginia, November 2-5, 1986. Contribution No. 805 of The Belle W. Baruch Institute.

Vapor Pressures and Gas-Phase *PVT* Data for 1,1-Dichloro-2,2,2-trifluoroethane

L. A. Weber

Thermophysics Division, Center for Chemical Technology, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

We present new data for the vapor pressure and gas-phase *PVT* surface of 1,1-dichloro-2,2,2-trifluoroethane (refrigerant 123) in the temperature range 338-453 K at densities up to 0.67 mol/L. The data have been represented analytically to demonstrate the precision and to facilitate calculation of thermodynamic properties.

Introduction

1,1-Dichloro-2,2,2-trifluoroethane (CCl_2HCF_3 or R 123) has been suggested as a possible substitute for CCl_3F (R11) for use in the blowing of polyurethane and phenolic foams. Since large quantities of these blowing agents are released directly into the atmosphere, it is desirable that they have a short atmospheric lifetime.