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Vapor Pressures and Enthalpies of Vaporization for Toxaphene Congeners

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Subcooled saturation liquid-phase vapor pressures (P_L) were determined for 21 chlorinated bornane and camphene congeners by capillary gas chromatography. Values of P_L for congeners with 6−10 chlorine substituents at 25 °C ranged from (0.23 to 7.1) mPa, and enthalpies of vaporization ($\Delta_{vap}H$) ranged from (77.6 to 91.8) kJ·mol^{-1}. Values of log P_L and $\Delta_{vap}H$ were inversely correlated to chlorine number (r^2 = 0.883 and 0.854). When correlated versus molecular mass, P_L values of toxaphene congeners were slightly lower than those of other nonaromatic chlorinated pesticides (hexachlorocyclohexanes, cyclodienes) but higher than P_L values of aromatic chlorinated pesticides (DDT group compounds) and polychlorinated biphenyls (PCBs). The $\Delta_{vap}H$ values of toxaphene congeners and other nonaromatic chlorinated pesticides were similar, and both groups of compounds had $\Delta_{vap}H$ values lower than those for DDTs and PCBs. Relationships of log P_L and $\Delta_{vap}H$ to chlorine positioning followed published trends with relative retention index on a nonpolar GC column.

Introduction

Toxaphene was used as a broad-spectrum insecticide in the United States until its deregistration for most applications in 1982 and withdrawal from all applications in 1986.[1] Over 80% of all applications occurred in the southern U.S.[2] Toxaphene and similar products were produced in other countries, including Nicaragua, Mexico, the former Soviet Union, and eastern Europe.[3] As one of the 12 persistent organic pollutants (POPs) targeted for global elimination under the UNEP Stockholm Convention,[4] new toxaphene applications are expected to cease.

Residues of toxaphene remain in agricultural soils and continue to volatilize into the atmosphere years after its deregistration.[5,6] Atmospheric transport and deposition of toxaphene into the Great Lakes[7−11] has resulted in contamination of fish, especially in Lake Superior.[12] Toxaphene is also prevalent in the Arctic, where it has been found in air and seawater[13−17] and in sediments of arctic and subarctic lakes.[18,19] Toxaphene is the most abundant organochlorine pesticide in the Canadian Arctic beluga whale and is prominent in fish from arctic lakes and marine waters.[20]

Investigations of toxaphene transport and fate are hampered by the lack of well-defined physicochemical properties. Most properties have been determined for technical toxaphene, a mixture of several hundred chlorinated bornanes (Figure 1) and camphenes,[21] and usually at a single temperature. The vapor pressure, water solubility, and Henry's law constant were reported at 20 °C for technical toxaphene,[22] and the Henry's law constant was also measured[23] over the range (10 to 35) °C. A range of vapor pressures for the components in technical toxaphene at 30 °C was reported.[24] Octanol−water partition coefficients (K_{ow}) for 36 toxaphene congeners and peaks in the technical mixture at 25 °C were determined.[25]

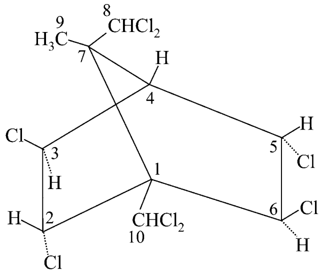

Figure 1. Structure of B8-1413 (enantiomer a), showing IUPAC numbering of the bornane carbons.[47]

Gas chromatography (GC), based on relative retention times (RRTs) or Kovat's retention indices, has been used to determine subcooled liquid saturation vapor pressures (P_L) for a wide variety of low and moderately polar substances. These applications were recently reviewed.[26] An advantage of the GC technique is that it is based on chromatographic separation, making it tolerant to impurities and allowing several compounds to be run simultaneously.

In the current study, capillary GC was used to determine the P_L values of 21 toxaphene congeners ranging in chlorine numbers from 6 to 10, and enthalpies of vaporization ($\Delta_{vap}H$) were calculated from the temperature dependence of P_L.

Experimental Section

Chemicals. Single chlorobornane and chlorocamphene congeners (Table 1) were purchased as solutions from Ehrenstorfer Laboratories (Augsburg, Germany) or Promochem, Inc. (Wesen, Germany) or were supplied by individual investigators (see Acknowledgment). Purities were not given, although the concentrations of solutions from Ehrenstorfer Labs were specified to have an accuracy of ±15%. Organochlorine pesticides were from the U.S. Environmental Protection Agency Repository for Pesticides

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Table 1. Toxaphene Congeners Used for Vapor Pressure Measurements

compd no.	type	no. of chlorines	chemical name	other designations[45−47]
1	camphene	6	5-*exo*,6-*endo*-dichloro-2-*endo*-chloromethyl-3-(*E*)-chloromethylene-2-dichloromethyl-8,9,10-trinorbornane	P12
2	bornane	6	2-*exo*,3-*endo*,6-*exo*,8,9,10-hexachlorobornane	B6-923, hex-sed
3	bornane	7	2-*exo*,5,5,9,9,10,10-heptachlorobornane	B7-1715
4	bornane	7	2,2,5,5,9,10,10-heptachlorobornane	B7-499, P21
5	bornane	7	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10-heptachlorobornane	B7-1001, hept-sed
6	camphene	7	2,2,3-*exo*-trichloro-5-*endo*-chloromethyl-6-(*E*)-chloromethylene-5-dichloromethyl-8,9,10-trinorbornane	P25
7	bornane	8	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-octachlorobornane	B8-1413, P26, T2
8	bornane	7	2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane	B7-515, P32, toxicant B
9	bornane	8	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10-octachlorobornane	B8-1412
10	bornane	7	2-*exo*,3-*endo*,6-*endo*,8,9,10,10-heptachlorobornane	B7-1462
11	camphene	8	2,2,3-*exo*-trichloro-6-(*E*)-chloromethylene-5,5-bis(dichloromethyl)-8,9,10-trinorbornane	P31
12	bornane	8	2,2,3-*exo*,5-*endo*,6-*exo*,8,9,10-octachlorobornane	B8-531, P39
13	bornane	8	2,2,5-*endo*,6-*exo*,8,8,9,10-octachlorobornane	B8-806, P42a toxicant A
14	bornane	8	2,2,5-*endo*,6-*exo*,8,9,9,10-octachlorobornane	B8-809, P42b toxicant A
15	bornane	8	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,9,10,10-octachlorobornane	B8-1414, P40
16	bornane	8	2-*exo*,5,5,8,9,9,10,10-octachlorobornane	B8-2229, P44
17	bornane	9	2,2,3-*exo*,5,5,9,9,10,10-nonachlorobornane	B9-718
18	bornane	9	2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-nonachlorobornane	B9-1679, P50, T12, toxicant Ac
19	bornane	9	2,2,5,5,8,9,9,10,10-nonachlorobornane	B9-1025, P62
20	bornane	9	2-*exo*,3-*endo*,5-*exo*,6-*exo*,8,8,9,10,10-nonachlorobornane	B9-2206, P63
21	bornane	10	2,2,5,5,6-*exo*,8,9,9,10,10-decachlorobornane	B10-1110, P69

and Industrial Chemicals (Research Triangle Park, NC). PCB congeners were from AccuStandard Corp. (New Haven, CT). Solvents were chromatographic quality.

Vapor Pressure Measurements. Determination of P_L by capillary GC was done according to a previously described technique.[27,28] The column was a DB-1 (poly(dimethylsiloxane), bonded phase, 1 m × 0.25 mm diameter, 0.25 μm film, J&W Scientific Co., Rancho Cordova, CA), installed in a Hewlett-Packard 5790 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD). The carrier gas was H_2 at a nominal flow of 4 $mL\cdot min^{-1}$ at ambient temperature. The flow rate probably varied slightly at the different oven temperatures used for the experiments; however, this was inconsequential, since the relative retention times of the test to the standard compound were measured. Nitrogen makeup gas was used for the ECD at 50 $mL\cdot min^{-1}$. Samples of (2 to 4) μL in petroleum ether were injected manually at a split/carrier ratio of 10:1 or 20:1. Injector and detector temperatures were 200 °C and 300 °C. Data were collected and integrated using HP Chemstation software.

Analytes were cochromatographed with a *p,p*′-DDT reference standard at a series of isothermal temperatures ranging from (70 to 130) °C. RRTs were very reproducible, with relative standard deviations for three to four replicates averaging 0.4%. Calculation of vapor pressures from retention data[27−31] was done using eqs 1 and 2. The natural logarithms of the test compounds retention times compared to those of *p,p*′-DDT (t_X/t_{ref}) were plotted versus the ln P_L of reference *p,p*′-DDT at the particular isothermal temperature[26−29]

$$\ln(t_X/t_{ref})_T = (1 - \Delta_{vap}H_X/\Delta_{vap}H_{DDT})\ \ln(P_{L,DDT}/Pa)_T - C \tag{1}$$

The regression yields the ratio of vaporization enthalpies for compound X and *p,p*′-DDT ($\Delta_{vap}H_X/\Delta_{vap}H_{DDT}$) and intercept *C*. An estimate of the GC-determined vapor pressure at 25 °C (P_{GC}) is calculated from this enthalpy ratio, the intercept *C*, and the vapor pressure of *p,p*′-DDT at 25 °C

$$\ln(P_{GC}/Pa)_{25} = (\Delta_{vap}H_X/\Delta_{vap}H_{DDT})\ \ln(P_{L,DDT}/Pa)_{25} + C \tag{2}$$

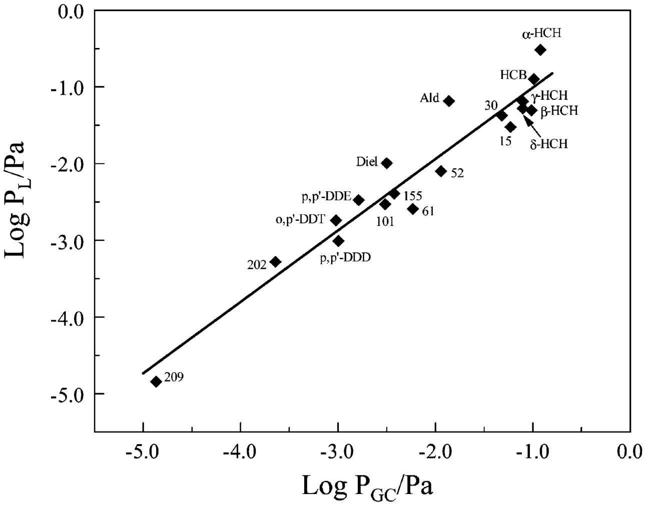

Figure 2. Calibration plot for estimating log P_L from log P_{GC}. Numbers indicate PCB congeners.

The solid-phase vapor pressure (P_S) of *p,p*′-DDT has been reported by five laboratories, with good agreement. Four of these measurements were summarized by Hinckley and co-workers.[28] The vapor pressure determined by Wania and co-workers[32] was included; the five results were averaged and converted to P_L using the experimentally determined entropy of fusion ($\Delta_{fus}S$) and melting point (392 K) for *p,p*′-DDT. Four reported values[28,33−36] of $\Delta_{fus}S$ were (68.8, 69.1, 71.2, and 74.5) $J\cdot mol^{-1}\cdot K^{-1}$, and the average value of 70.9 $J\cdot mol^{-1}\cdot K^{-1}$ was selected. The equation for P_L of *p,p*′-DDT as a function of temperature was

$$\log(P_L/Pa)_{DDT} = 12.38\ (\pm\ 0.48) - 4665\ (\pm\ 166)/T \tag{3}$$

A calibration plot (Figure 2) was prepared of log P_L versus log P_{GC} at 25 °C, using P_L values of organochlorine compounds whose vapor pressures had been measured by methods other than GC:[27,28,32,33] hexachlorobenzene (HCB), four isomers of hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH, δ-HCH), aldrin, dieldrin, *p,p*′-DDE, *o,p*′-DDT, *p,p*′-DDD, and PCB congeners 15, 30, 52, 61, 101, 155, 202, and 209 (IUPAC). Conversion from P_S to P_L for the calibration compounds was done using experimentally determined $\Delta_{fus}S$ values where available;[28,34,35,37] otherwise, a default value[28] of $\Delta_{fus}S = 56.5\ J{\cdot}mol^{-1}{\cdot}K^{-1}$ was used. The regression equation for the calibration plot ($r^2 = 0.925$) was

$$\log P_L/\mathrm{Pa} = 0.931\ (\pm\ 0.066) \log P_{GC}/\mathrm{Pa} - 0.078\ (\pm\ 0.158) \quad (4)$$

This calibration plot was used to calculate P_L values of toxaphene congeners from their measured P_{GC} values at 25 °C. The temperature dependence of P_L for congener X was

$$\log(P_L/\mathrm{Pa}) = m_X/T + b_X \quad (5)$$

where $m_X = -\Delta_{vap}H_X/2.303R$; $\Delta_{vap}H_X$ was calculated from the enthalpy ratio ($\Delta_{vap}H_X/\Delta_{vap}H_{DDT}$) and $\Delta_{vap}H_{DDT}$.

Results and Discussion

Vapor Pressure Estimation and Calibration. The GC method assumes that the activity coefficients of test chemicals and *p,p′*-DDT are the same in the GC stationary phase, which may not be true. In particular, the activity coefficients for nonpolar chemicals may vary systematically with molecular mass, and correction for this effect must be made.[29] Puri et al.[38] addressed this problem by cochromatographing a series of standards with the test chemicals. Another approach, taken by ourselves[27,28] and others,[29−31] is to prepare a log−log calibration plot of P_L versus P_{GC}, using a series of chemicals whose vapor pressures have been determined by methods other than GC.

The error in converting P_{GC} to P_L depends only slightly on uncertainties in the measured relative retention times, which are ~0.4%, as mentioned in the Experimental Section. For the most part, errors are associated with uncertainties in the literature values of P_L for chemicals used to prepare the calibration plot. These P_L values often vary by a factor of 2 or more.[27,28,32,39,40] To this is added the uncertainty in $\Delta_{fus}S$ (e.g., see earlier for *p,p′*-DDT), which is needed to convert P_S to P_L.

The log−log plot of P_L versus P_{GC} (eq 4) has a standard error of estimate (S_e) = 0.29. The standard error of prediction (S_p) of log P_L from P_{GC} can be estimated from[41]

$$S_p^{\,2} = S_e^{\,2}\left[1 + 1/n + \frac{(\bar{X} - X_i)^2}{\sum X_i^{\,2} - n\bar{X}^{\,2}}\right] \quad (6)$$

where X_i and $\bar{X}$ are individual and average log P_{GC} and n is the number of points in the calibration plot. Values of S_p for log P_L ranged from 0.30 to 0.34 for the toxaphene congeners (Table 2), corresponding to an uncertainty of about a factor of 2 in P_L.

Vapor Pressures and Vaporization Enthalpies of Toxaphene Congeners. The P_L values of the 21 toxaphene congeners decrease from 7.1 mPa for hexachlorocamphene P12 to 0.22 mPa for decachlorobornane B10-1110 (Table 2). Hinckley et al.[28] reported P_L for B7-515 (2.1 mPa) and the coeluting compounds B8-806 and B8-809 (1.1 mPa) at 25 °C using the GC technique and a calibration plot prepared with both organochlorine and polycyclic aromatic hydrocarbon standard compounds. These compare with 2.8 mPa for B7-515 and 1.5 mPa for B8-806 and B8-809 determined in this work, using a calibration plot with only organochlorines. Murphy et al.[22] measured $P_S = 0.89$ mPa for toxaphene at 20 °C by headspace analysis of air in equilibrium with solid technical toxaphene (mp 65−90 °C). Since the analysis was based on total peak area, this result is biased toward the more volatile components of the technical toxaphene mixture. Seiber et al.[24] reported a wider range of vapor pressure values at 30 °C for the components of technical toxaphene: 5.5 μPa to 6.0 mPa, with an average = 0.13 mPa and the values for major components ranging from 44 μPa to 0.40 mPa. The method employed chromatography of toxaphene on a standard-length analytical column (25−30 m) at an elevated (though not specified) temperature along with a series of chlorinated pesticide standards, all of which have higher melting points than that of technical toxaphene. The comparison was made using the P_S values of these pesticides, so it is unclear whether the above vapor pressures for toxaphene are P_S, P_L, or somewhere in between.

Table 2. Vapor Pressures and Enthalpies of Vaporization of Toxaphene Congeners[a,b]

compd no.	congener	log P_L/Pa	m	b	$\Delta_{vap}H$/ kJ·mol^{-1}
1	P12	−2.15 (0.32)	−4075	11.51	78.0 (2.8)
2	B6-923	−2.18 (0.32)	−4058	11.43	77.7 (2.8)
3	B7-1715	−2.23 (0.31)	−4054	11.37	77.6 (2.8)
4	B7-499	−2.28 (0.31)	−4083	11.42	78.2 (2.8)
5	B7-1001	−2.36 (0.31)	−4171	11.63	79.9 (2.8)
6	P25	−2.54 (0.30)	−4315	11.93	82.6 (2.9)
7	B8-1413	−2.55 (0.30)	−4258	11.73	81.5 (2.9)
8	B7-515	−2.55 (0.30)	−4234	11.65	81.1 (2.9)
9	B8-1412	−2.58 (0.30)	−4262	11.72	81.6 (2.9)
10	B7-1462	−2.63 (0.30)	−4275	11.71	81.9 (2.9)
11	P31	−2.67 (0.30)	−4327	11.85	82.8 (3.0)
12	B8-531	−2.79 (0.30)	−4359	11.84	83.5 (3.0)
13	B8-806	−2.82 (0.30)	−4383	11.88	83.9 (3.0)
14	B8-809	−2.82 (0.30)	−4383	11.88	83.9 (3.0)
15	B8-1414	−2.83 (0.30)	−4388	11.89	84.0 (3.0)
16	B8-2229	−2.84 (0.30)	−4385	11.87	84.0 (3.0)
17	B9-718	−3.01 (0.31)	−4450	11.92	85.2 (3.0)
18	B9-1679	−3.06 (0.31)	−4526	12.12	86.7 (3.1)
19	B9-1025	−3.22 (0.31)	−4563	12.09	87.4 (3.1)
20	B9-2206	−3.32 (0.32)	−4625	12.19	88.6 (3.2)
21	B10-1110	−3.64 (0.34)	−4795	12.44	91.8 (3.3)

[a] At 25 °C. [b] The values in parentheses are the standard errors (s.e.). Those for log P_L were estimated from eq 6, and those for $\Delta_{vap}H$ were estimated from the variation in $\Delta_{vap}H_{DDT}$ (see text).

The $\Delta_{vap}H$ values for the 21 toxaphene congeners ranged from (77.6 to 91.8) kJ·mol^{-1} (Table 2). Uncertainties in $\Delta_{vap}H$ are due to errors in the slope of eq 2 and in $\Delta_{vap}H_{DDT}$. Propagation of errors shows that over 95% of the uncertainty in $\Delta_{vap}H$ for the toxaphene congeners is due to the relative error in $\Delta_{vap}H_{DDT}$, which is 3.2% (eq 3), and this is reflected in the precision of $\Delta_{vap}H$ reported in Table 2.

Relationships to Chlorine Number and Molecular Mass. Values of log P_L and $\Delta_{vap}H$ are related to the number of chlorines (Cl) (Figure 3) and to each other and by

$$\log P_L/\mathrm{Pa} = -0.354(\mathrm{Cl}) + 0.044 \quad (7)$$

$$\Delta_{vap}H/\mathrm{kJ{\cdot}mol^{-1}} = 3.32(\mathrm{Cl}) + 57.00 \quad (8)$$

$$\Delta_{vap}H/\mathrm{kJ{\cdot}mol^{-1}} = -9.37 \log P_L/\mathrm{Pa} + 57.16 \quad (9)$$

The r^2 values for eqs 7−9 are 0.883, 0.854, and 0.986, respectively. Fisk and co-workers[25] determined K_{ow} for 36 chromatographic peaks in technical toxaphene. Analysis by GC−NIMS allowed the chlorination level of each component to be determined. Log K_{ow} was positively correlated with chlorine number, but at a lower $r^2 = 0.44$ than that for the volatility-related properties studied here.

Figure 4 shows log P_L and $\Delta_{vap}H$ values for different classes of chlorinated compounds in relation to their

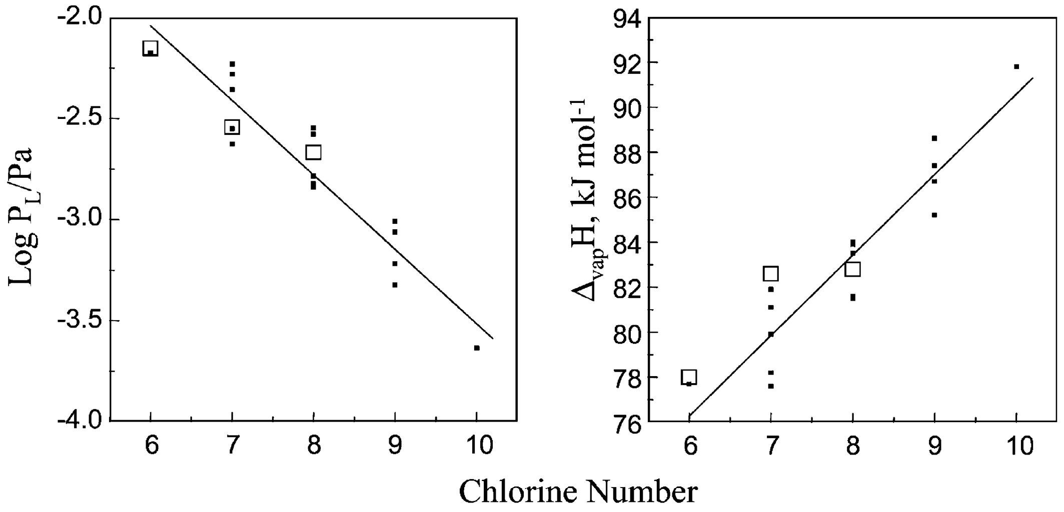

Figure 3. Relationships of chlorine number to (a) log P_L ($r^2 = 0.882$) and (b) $\Delta_{vap}H$ ($r^2 = 0.855$): black squares, chlorobornanes; open squares, chlorocamphenes.

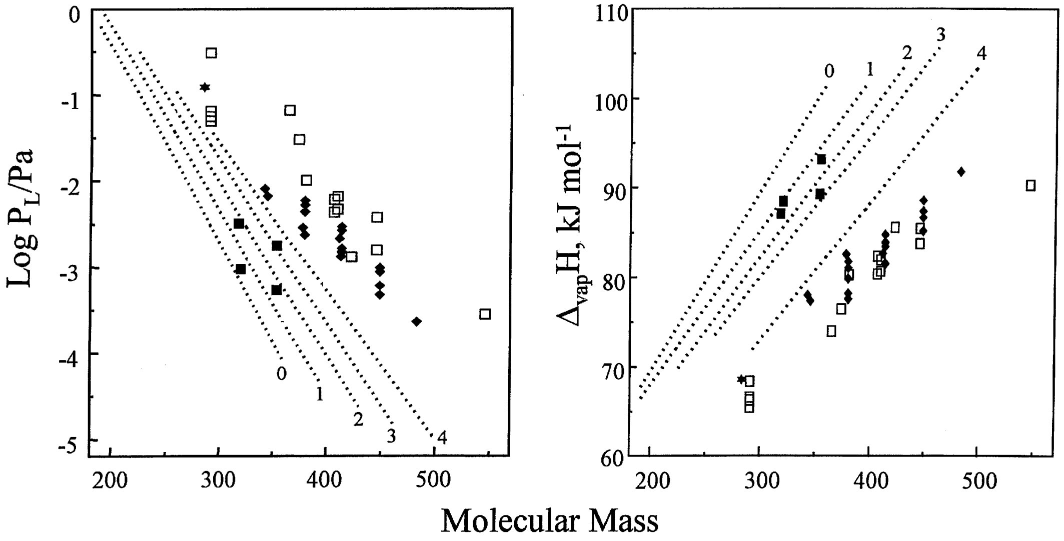

Figure 4. Relationships of molecular mass to (a) log P_L and (b) $\Delta_{vap}H$ for different classes of chlorinated organic compounds: black diamonds (this work), toxaphene congeners; black squares, DDT compounds (*p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE),[28] open squares, nonaromatic organochlorine pesticides (hexachlorocyclohexanes, heptachlor, chlordanes, nonachlors, aldrin, dieldrin, endosulfan, endosulfan sulfate, mirex),[28] black star, hexachlorobenzene (HCB). Numbered lines indicate properties for PCBs having different *o*-chlorine substitutions.[42]

molecular masses. The toxaphene congeners are plotted as one class. Another group comprises the nonaromatic chlorinated pesticides hexachlorocyclohexanes (HCHs), heptachlor, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, endosulfan I and II, endosulfan sulfate, aldrin, dieldrin, and mirex, whose properties were calculated from the eq 4 parameters reported by Hinckley et al.[28] and/or determined in this study. The aromatic DDT compounds are plotted separately (data also from Hinckley et al.[28]). For polychlorinated biphenyls (PCBs), P_L and $\Delta_{vap}H$ vary with homologue and also with the number of ortho-substituted chlorines.[38,42] The PCB lines in Figure 4 are from the parameters reported by Falconer and Bidleman[42] for eq 4. The $\Delta_{vap}H$ values of Puri et al.[38] also show a dependence on molecular mass and *o*-chlorine substitution, but they are about 6 to 7 kJ·mol^{-1} higher.

For compounds of the same molecular mass, P_L is lower and $\Delta_{vap}H$ is higher for diaromatic compounds (PCBs and DDTs) than for nonaromatic chlorinated pesticides. The $\Delta_{vap}H$ values of the toxaphene congeners are close to those of other nonaromatic chlorinated pesticides, while their P_L values are slightly lower. The monoaromatic compound HCB falls in with the nonaromatic chlorinated pesticides, having P_L and $\Delta_{vap}H$ values similar to those of the HCHs.

Relationship of Properties to Toxaphene Structure. Figures 3 and 4 show that although chlorine number or molecular mass exerts the largest effect on P_L and $\Delta_{vap}H$, there is variation within a homologue and overlap for some adjacent homologues (e.g., heptachloro- and octachloro-compounds), indicating that the substitution pattern is also important in determining these physicochemical properties.

Vetter et al.[43] separated toxaphene congeners on a nonpolar CP-Sil 2 phase and noted the influence of certain structural features on relative retention indices (RRI). Substitutions that favored early elution (low RRI) were chlorines at the 8,8 or 9,9 (or either 8 or 9 alone) positions and alternating 2-endo,3-exo,5-endo,6-exo chlorine substitution in the ring (referred to as endo−exo) (see Figure 1 for the IUPAC numbering scheme). Late elution (high RRI) was associated with 8,9 substitution.

Similar trends can be seen in the results from this study when the chlorobornanes are grouped by homologue (Table

Table 3. Toxaphene Properties in Relation to Chlorine Substitution[a]

congener	chlorines on C8 and C9	endo−exo substitution[b]	$\Delta_{vap}H$ kJ·mol^{-1}	$\Delta_{form}H$ kJ·mol^{-1}	P_L mPa
B7-1715	9,9	N	77.6		5.89
B7-499	9	N	78.2		5.25
B7-1001	8,9	Y	79.9	−243.5	4.37
B7-515	8,9	N	81.1	−218.8	2.82
B7-1462	8,9	N	81.9		2.34
B8-1413	8,8	Y	81.5	−230.6	2.82
B8-1412	8,8,9	Y	81.6	−244.4	2.63
B8-531	8,9	N	83.5		1.62
B8-806	8,8,9	N	83.9	−209.8	1.51
B8-809	8,9,9	N	83.9	−216.5	1.51
B8-1414	8,9	N	84.0	−245.9	1.48
B8-2229	8,9,9	N	84.0	−206.8	1.45
B9-718	9,9	N	85.2		0.98
B9-1679	8,8,9	Y	86.7	−245.7	0.87
B9-1025	8,9,9	N	87.4	−187.7	0.60
B9-2206	8,8,9	N	88.6		0.48

[a] $\Delta_{form}H$ from Vetter and Schurig.[47] [b] Y, chlorines in all of the 2-endo,3-exo,5-endo,6-exo positions; N, other substitutions.

3). Five 7-Cl bornanes were examined. B7-1715 and B7-499 with 9,9 and 9 substitution have higher P_L (5.3 to 5.9 mPa) and lower $\Delta_{vap}H$ (77.6 to 78.2 kJ·mol^{-1}) than B7-1001, B7-515, and B7-1462 (P_L = 2.3 to 4.4 mPa; $\Delta_{vap}H$ = 79.9 to 81.9 kJ·mol^{-1}), which have 8,9 substitution. Within the latter group of three congeners, B7-1001 with endo−exo substitution has the highest P_L (4.4 mPa) and lowest $\Delta_{vap}H$ (79.9 kJ·mol^{-1}). Among the seven 8-Cl bornanes, B8-1413 and B8-1412 have higher P_L (2.6 to 2.8 mPa) and lower $\Delta_{vap}H$ (81.5 to 81.6 kJ·mol^{-1}). These congeners have chlorines in the 8,8 or 8,8,9 positions and endo−exo substitution. The other five congeners (B8-531, B8-806, B8-809, B8-1414, and B8-2229) have either 8,9; 8,9,9; or 8,9,9 chlorine positioning and no endo−exo substitution. These five congeners have similar properties (P_L = 1.5 to 1.6 mPa; $\Delta_{vap}H$ = 83.5 to 84.0 kJ·mol^{-1}). Of the four 9-Cl bornanes, congeners B9-718 (9,9) and B9-1679 (8,8,9 and endo−exo substitution) have higher P_L (0.87 to 0.98 mPa) and lower $\Delta_{vap}H$ (85.2 to 86.7 kJ·mol^{-1}) than the other two congeners (B9-1025 and B9-2206) with lower P_L (0.48 to 0.60 mPa) and higher $\Delta_{vap}H$ (87.4 to 88.6 kJ·mol^{-1}), which have chlorines in the 8,9,9 or 8,8,9 positions and no endo−exo substitution.

The endo−exo chlorine substitution has been associated with chlorobornanes of greater environmental persistence and more negative enthalpy of formation ($\Delta_{form}H$).[44] A possible relationship of $\Delta_{vap}H$ to $\Delta_{form}H$ was examined for 10 chlorobornanes whose $\Delta_{form}H$ values were reported by Vetter and Scherer,[44] five with endo−exo and five with other ring substitutions (Table 3). No significant correlation was obtained ($p = 0.24$).

Three of the congeners examined have camphene backbones (compounds 1, 6, and 11 in Table 1), and these are plotted as separate symbols in Figure 3. No apparent differences in properties could be discerned for these compared to the chlorobornanes.

Although structure does affect the physicochemical properties of toxaphene congeners, there is limited opportunity to explore these relationships with only 21 congeners. A more comprehensive study which includes molecular modeling would be desirable.

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Literature Cited

(1) U. S. Environmental Protection Agency. Toxaphene: Intent to Cancel or Restrict Registrations of Pesticide Products Containing Toxaphene. *Fed. Regist.* **1982**, *47*, 53784−53793.
(2) Li, Y.-F. Toxaphene in the United States: 1. Usage gridding. *J. Geophys. Res.* **2001**, *106* (D16), 17919−17927.
(3) Pesticide Action Network (PAN). *Demise of the Dirty Dozen*; North American Regional Center for PAN International: San Francisco, CA, 1995.
(4) United Nations Environmental Program (UNEP). Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. UNEP, Geneva, Switzerland, 2001; 44 pages.
(5) Harner, T.; Jantunen, L. M.; Bidleman, T. F.; Mackay, D. Soil-Air Exchange Model of Persistent Pesticides in the United States Cotton Belt. *Environ. Toxicol. Chem.* **2001**, *20*, 1612−1621.
(6) Li, Y.-F.; Bidleman, T. F.; Barrie, L. A. Toxaphene in the United States: 2. Emissions and Residues. *J. Geophys. Res.* **2001**, *106* (D16), 17929−17938.
(7) James, R. R.; Hites, R. A. Atmospheric Transport of Toxaphene from the Southern United States to the Great Lakes Region. *Environ. Sci. Technol.* **2002**, *36*, 3474−3481.
(8) James, R. R.; McDonald, J. G.; Symonik, D. M.; Swackhamer, D. L.; Hites, R. A. Volatilization of Toxaphene from Lakes Michigan and Superior. *Environ. Sci. Technol.* **2001**, *35*, 3653−3660.
(9) Jantunen, L. M.; Bidleman, T. F. Air−Water Gas Exchange of Toxaphene in Lake Superior. *Environ. Toxicol. Chem.* **2003**, *22*, 1229−1237.
(10) Shoeib, M.; Brice, K. A.; Hoff, R. M. Airborne Concentration of Toxaphene Congeners at Point Petre (Ontario) Using Gas Chromatography−Electron Capture Negative Ion Mass Spectrometry (GC-ECNIMS). *Chemosphere* **1999**, *39*, 849−871.
(11) Swackhamer, D. L.; Schottler, S.; Pearson, R. F. Air−Water Exchange and Mass Balance of Toxaphene in the Great Lakes. *Environ. Sci. Technol.* **1999**, *33*, 3864−3872.
(12) Glassmeyer, S. T.; DeVault, D. S.; Meyer, T. R.; Hites, R. A. Rates at which Toxaphene Concentrations Decrease in Lake Trout from the Great Lakes. *Environ. Sci. Technol.* **2000**, *34*, 1851−1855.
(13) Bidleman, T. F.; Falconer, R. L.; Walla, M. D. Toxaphene and Other Organochlorine Compounds in Air and Water at Resolute Bay, N.W.T., Canada. *Sci. Total Environ.* **1995**, *160/161*, 55−63.
(14) Jantunen, L. M. Air−Water Gas Exchange of Toxaphene in Arctic Regions. M.A.Sc. Thesis, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON, Canada, 1997, 88 pages.
(15) Jantunen, L. M.; Bidleman, T. F. Organochlorine Pesticides and Enantiomers of Chiral Pesticides in Arctic Ocean Water. *Arch. Environ. Contam. Toxicol.* **1998**, *35*, 218−228.
(16) Patton, G. W.; Walla, M. D.; Bidleman, T. F.; Barrie, L. A. Polycyclic Aromatic and Organochlorine Compounds in the Atmosphere of Northern Ellesmere Island, Canada. *J. Geophys. Res.* **1991**, *96*, 10867−10877.
(17) Patton, G. W.; Hinckley, D. A.; Walla, M. D.; Bidleman, T. F. Airborne Organochlorines in the Canadian High Arctic. *Tellus* **1989**, *41B*, 243−255.
(18) Muir, D. C. G.; Grift, N. P.; Lockhart, W. L.; Wilkinson, P.; Billeck, B. N.; Brunskill, G. J. Spatial Trends and Historical Profiles of Organochlorine Pesticides in Arctic Lake Sediments. *Sci. Total Environ.* **1995**, *160/161*, 447−457.
(19) Rawn, D. F. K.; Lockhart, W. L.; Wilkinson, P.; Savoie, D. A.; Rosenberg, B.; Muir, D. C. G. Historical Contamination of Yukon Sediments by PCBs and Organochlorine Pesticides: Influence of Local Sources and Watershed Characteristics. *Sci. Total Environ.* **2001**, *280*, 17−37.
(20) Muir, D.; Braune, B.; DeMarch, B.; Norstrom, R.; Wagemann, R.; Lockhart, L.; Hargrave, B.; Bright, D.; Addison, R.; Payne, J.; Reimier, K. Spatial and Temporal Trends and Effects of Contaminants in the Canadian Arctic Marine Ecosystem: A Review. *Sci. Total Environ.* **1999**, *230*, 83−144.
(21) Hainzl, D.; Burhenne, J.; Parlar, H. Theoretical Consideration of the Structural Variety in the Toxaphene Mixture Taking into Account Recent Experimental Results. *Chemosphere* **1994**, *28*, 245−251.
(22) Murphy, T. J.; Mullen, M. D.; Meyer, J. A. Equilibration of Polychlorinated Biphenyls and Toxaphene with Air and Water. *Environ. Sci. Technol.* **1987**, *21*, 155−162.

(23) Jantunen, L. M.; Bidleman, T. F. Temperature-Dependent Henry's Law Constant for Technical Toxaphene. *Chemosphere: Global Change Sci.* **2000**, *2*, 225−231.

(24) Seiber, J. N.; Woodrow, J. E.; Sanders, P. F. Estimation of Ambient Vapor Pressures of Pesticides from Gas Chromatographic Retention Data. Presented at the 182nd American Chemical Society meeting, New York, 1981.

(25) Fisk, A. T.; Rosenberg, B.; Cymbalisty, C. D.; Stern, G. A.; Muir, D. C. G. Octanol−Water Partition Coefficients of Toxaphene Congeners Determined by the "Slow-Stirring" Method. *Chemosphere* **1999**, *39*, 2549−2562.

(26) Koutek, B.; Cvačka, J.; Streinz, L.; Vrkočova, P.; Doubský, J.; Šimonova, H.; Feltl, L.; Svoboda, V. Comparison of Methods Employing Gas Chromatography Retention Data to Determine Vapour Pressures at 298 K. *J. Chromatogr.* **2001**, *923*, 137−152.

(27) Bidleman, T. F. Estimation of Vapor Pressures for Nonpolar Organic Compounds by Capillary Gas Chromatography. *Anal. Chem.* **1984**, *56*, 2490−2496.

(28) Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T.; Tuschall, J. R. Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data. *J. Chem. Eng. Data* **1990**, *35*, 232−237.

(29) Lei, Y. D.; Wania, F.; Shiu, W.-Y. Vapor Pressures of the Polychlorinated Naphthalenes. *J. Chem. Eng. Data* **1999**, *44*, 577−582.

(30) Lei, Y. D.; Chankalal, R.; Chan, A.; Wania, F. Super-Cooled Liquid Vapor Pressures of the Polycyclic Aromatic Hydrocarbons. *J. Chem. Eng. Data* **2002**, *47*, 801−806.

(31) Wong, A.; Lei, Y. D.; Alaee, M.; Wania, F. Vapor Pressures of the Polybrominated Diphenyl Ethers. *J. Chem. Eng. Data* **2001**, *46*, 239−242.

(32) Wania, F.; Shiu, W.-Y.; Mackay, D. Measurement of the Vapor Pressure of Several Low-Volatility Organochlorine Chemicals at Low Temperatures with a Gas Saturation Method. *J. Chem. Eng. Data* **1994**, *39*, 572−577.

(33) Balson, E. W. Studies in Vapour Pressure Measurement, part III. An Effusion Manometer Sensitive to 5×10^{-6} Millimeters of Mercury: Vapour Pressure of DDT and Other Slightly Volatile Substances. *Trans. Faraday Soc.* **1947**, *43*, 54−60.

(34) Plato, C.; Glasgow, A. R., Jr. Differential Scanning Calorimetry as a General Method for Determining Purity and Heat of Fusion of High-Purity Organic Chemicals. Application to 95 Compounds. *Anal. Chem.* **1969**, *41*, 330−336.

(35) Donnelly, J. R.; Drewes, L. A.; Johnson, R. L.; Munslow, W. D.; Knapp, K. K.; Sovocool, G. W. Purity and Heat of Fusion Data for Environmental Standards as Determined by Differential Scanning Calorimetry. *Thermochim. Acta* **1990**, *167*, 155−187.

(36) 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. The chemical composition of technical DDT. *J. Am. Chem. Soc.* **1945**, *67*, 1591−1602.

(37) Plato, C. Differential Scanning Calorimetry as a General Method for Determining Purity and Heat of Fusion of High-Purity Organic Chemicals. Application to 64 Compounds. *Anal. Chem.* **1972**, *44*, 1531−1534.

(38) Puri, S.; Chickos, J. S.; Welsh, W. J. Determination of Vaporization Enthalpies of Polychlorinated Biphenyls Using Correlation Gas Chromatography. *Anal. Chem.* **2001**, *73*, 1480−1484.

(39) Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume 5, Pesticide Chemicals*; Lewis Publishers: Chelsea, 1997; 812 pages.

(40) Suntio, L. R.; Shiu, W.-Y.; Mackay, D.; Seiber, J. N. Critical Review of Henry's Law Constants for Pesticides. *Rev. Environ. Contam. Toxicol.* **1988**, *103*, 1−59.

(41) Levin, R. I.; Rubin, D. S. *Applied Elementary Statistics*; Prentice-Hall: Englewood Cliffs, NJ, 1980.

(42) Falconer, R. L.; Bidleman, T. F. Vapor Pressures and Predicted Particle/Gas Distributions of Polychlorinated Biphenyl Congeners as Functions of Temperature and Ortho-Chlorine Substitution. *Atmos. Environ.* **1994**, *28*, 547−554.

(43) Vetter, W.; Klobes, U.; Krock, B.; Luckas, B. Congener-Specific Separation of Compounds of Technical Toxaphene on a Nonpolar CP−Sil 2 Phase. *J. Microchem. Sep.* **1997**, *9*, 29−36.

(44) Vetter, W.; Scherer, G. Persistency of Toxaphene Components in Mammals that Can Be Explained by Molecular Modeling. *Environ. Sci. Technol.* **1999**, *33*, 3458−3461.

(45) Andrews, P.; Vetter, W. A. Systematic Nomenclature for Toxaphene Congeners. Part 1. Chlorinated Bornanes. *Chemosphere* **1995**, *31*, 3879.

(46) Coelhan, M.; Parlar. H. The Nomenclature of Chlorinated Bornanes and Camphenes Relevent to Toxaphene. *Chemosphere* **1996**, *32*, 217−228.

(47) Vetter, W.; Oehme, M. 2000. Toxaphene: Analysis and Environmental Fate of Congeners. In *Handbook of Environmental Chemistry, Vol. 3, Part K, New Types of Persistent Halogenated Compounds*; Paasivirta, J., Ed.; Springer-Verlag: Berlin, 2000; pp 237−287.

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