Note

Determination of polychlorinated biphenyl vapor pressures by capillary gas chromatography

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Transport of organic pollutants through the environment is, to a large extent, governed by two physical properties: water solubility and vapor pressure. For an important class of organic pollulant, polychlorinated biphenyls (PCBs), water solubilities have been determined for individual isomers. Vapor pressures, however, have been determined only for commercial Aroclor® fluids[2]. These mixtures contain fifteen or more isomers. For several reasons vapor pressure data for these mixtures are uncertain; there is no evidence that solutions of PCB isomers exhibit ideal behavior (obey Raoult's Law); vapor pressures for these mixtures at 25°C are extrapolated from data obtained at 100–250°C higher than room temperature; and finally, commercial PCB mixtures are liquids while most of the pure isomers are solids.

Gas chromatography has several advantages as a technique for determining vapor pressures: speed, tolerance to relatively impure compounds, the ability to determine vapor pressures of several compounds simultaneously, and small sample size requirements. This paper reports the use of glass capillary gas chromatography for determining the vapor pressures of individual PCB isomers and chlorinated pesticides.

THEORY

Vapor pressures for two substances at the same temperature are related through the equation:

$$\ln p_1{}^0 = L_1/L_2 \ln p_2{}^0 + C \tag{1}$$

where 1 and 2 refer to the test and reference compounds respectively, p^0 is the vapor pressure, L is the heat of vaporization, and C is a constant. The ratio L_1/L_2 and the constant C may be calculated from the relative retention volume (V_R) (or time) of the test to the reference compound and the vapor pressure of the reference compound:

$$\ln (V_R)_1/(V_R)_2 = (1 - L_1/L_2) \ln p_2{}^0 - C \tag{2}$$

A plot of $\ln (V_R)_1/(V_R)_2$ *vs.* $\ln p_2{}^0$ should give a straight line with slope $(1 - L_1/L_2)$

and intercept $-C$. It is assumed that the ratio of the heats of vaporization of the two compounds is independent of temperature over the range of measurements. The derivation of eqns. 1 and 2 is presented in detail by Hamilton[3].

EXPERIMENTAL

Nanogram quantities of individual PCB isomers in hexane were injected directly onto a 1 m × 0.25 mm I.D. wall-coated open tubular (WCOT) glass capillary column installed in a Varian 3700 gas chromatograph. Use of pentane as a solvent instead of hexane produced no difference in retention times. The stationary phase was Apolane-87 (Applied Science Labs., State College, PA, U.S.A.), chosen because of its low polarity and non-chiral structure. Hydrogen at a flow-rate of 2–4 ml/min was used as a carrier gas, and nitrogen at 30 ml/min was used as a make-up gas for the ^{63}Ni electron-capture detector. The column was operated isothermally at 60–130°C. Temperatures indicated by the oven pyrometer agreed well with those measured with a mercury thermometer inserted into the oven. The detector was maintained at 325°C, and the injector at 180°C. Retention times were measured in chart units from the injection point and were expressed relative to the retention time of 2,4,5-trichlorophenoxyacetic acid, isobutyl ester (2,4,5-TIB) which has a vapor pressure of $2.2 \cdot 10^{-5}$ Torr at 25°C[3]. PCB isomers were purchased from Analabs (North Haven, CT, U.S.A.). Pesticides were obtained from the U.S. Environmental Protection Agency Pesticide Repository (Research Triangle Park, NC, U.S.A.). Solvents were pesticide residue quality.

RESULTS

Vapor pressures for the reference compound, 2,4,5-TIB, in the temperature range of our measurements were obtained from Hamilton's relative retention data[3] for 2,4,5-TIB and dibutyl phthalate (DBP). Using his values for L_1/L_2 and C for the 2,4,5-TIB/DBP pair together with DBP vapor pressures at different temperatures (from the equation of Small et al.[4], quoted by Hamilton[3]), p^0 was calculated for 2,4,5-TIB in our temperature range using eqn. 1. Regression lines were fitted to ln $(V_R)_1/(V_R)_2$ vs. ln p_2^0 plots (Fig. 1) according to eqn. 2 and the parameters L_1/L_2 and C were obtained for each of the test compound/2,4,5-TIB pairs. Two to seven of these plots were constructed for each test compound. Table I gives, for each test compound, the means of the individual regression results for L_1/L_2 and C, and the means of the vapor pressure values calculated from the individual regression results and the vapor pressure for 2,4,5-TIB ($2.2 \cdot 10^{-5}$ Torr at 25°C; $4.1 \cdot 10^{-5}$ Torr at 30°C) using eqn. 1.

DISCUSSION

Selectivity in gas–liquid chromatography is influenced by the volatility of the solute and by chemical interactions between the solute and the stationary phase. If chemical effects can be eliminated or at least minimized, partitioning between the stationary and mobile phases is controlled by solute volatility. Non-polar columns have been employed in several applications involving determinations of boiling points
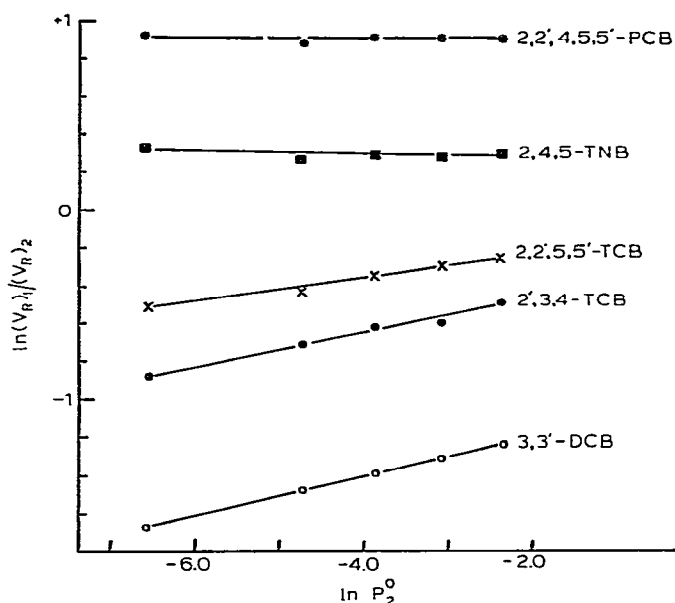
Fig. 1. Plots of ln $(V_R)_1/(V_R)_2$ vs. ln $p_2{}^0$ (vapor pressure of 2,4,5-TIB at different temperatures) for PCB isomers and 2,4,5-trichlorophenoxyacetic acid, *n*-butyl ester (2,4,5-TNB).

TABLE I

MEAN VALUES OF L_1/L_2, C, AND VAPOR PRESSURE

Compound	Experiments	L_1/L_2	C	p^0 (Torr) (25°C)
Pesticides				
p,p'-DDE	2	1.008 ± 0.063	-1.046 ± 0.270	$(7.4 \pm 2.7) \cdot 10^{-6}$
o,p'-DDT	2	1.030 ± 0.027	-1.312 ± 0.047	$(4.5 \pm 1.3) \cdot 10^{-6}$
2,4,5-T, *n*-butyl ester	7	1.016 ± 0.020	-0.222 ± 0.059	$(1.6 \pm 0.2) \cdot 10^{-5}$
PCB isomers				
3,3'-DCB	5	0.884 ± 0.029	0.900 ± 0.100	$(2.0 \pm 0.5) \cdot 10^{-4}$
2',3,4-TCB	4	0.913 ± 0.016	0.324 ± 0.056	$(8.0 \pm 1.0) \cdot 10^{-5}$
2,2',5,5'-TCB	4	0.925 ± 0.009	0.076 ± 0.039	$(5.5 \pm 0.4) \cdot 10^{-5}$
2,2',4,5,5'-PCB	4	1.000 ± 0.036	-0.897 ± 0.128	$(9.2 \pm 2.3) \cdot 10^{-6}$
2,2',4,4',6,6'-HCB	3	0.975 ± 0.029	-0.828 ± 0.113	$(1.2 \pm 0.2) \cdot 10^{-5}$

or vapor pressures. Packed columns with SE-30 as the stationary phase have been used by Green *et al.*[5] to simulate distillation of hydrocarbons, by Martin *et al.*[6] to calculate boiling points of phenothiazines, and by Hamilton[3] to determine vapor pressures of herbicides. Castello and D'Amato[7,8] found some variation in activity coefficient due to solute–solvent interactions when using SF-96 as a stationary phase to determine the vapor pressures of a series of alkanes.

Use of an open tubular column eliminates adsorption effects due to the presence of a stationary phase support. Stationary phase selectivity can be minimized by choosing a stationary phase of as low polarity as possible. Apolane-87 is an 87-unit

TABLE II

APOLANE-87: STRUCTURE AND McREYNOLDS CONSTANT
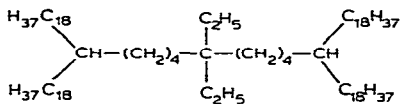
Phase	McReynolds constants*
Apolane-87	71
SF-96	205
SE-30	217

* Sum of five ΔI values (Applied Science Labs.).

hydrocarbon which is non-polar and non-chiral, with McReynolds constants lower than those for either SE-30 or SF-96 (Table II). The 1-m long WCOT column used for these experiments was obviously of lower efficiency than the 30–50-m columns normally used for analytical separations, but the ability to resolve large numbers of compounds of similar volatility is not a major requirement for this technique. Fig. 2
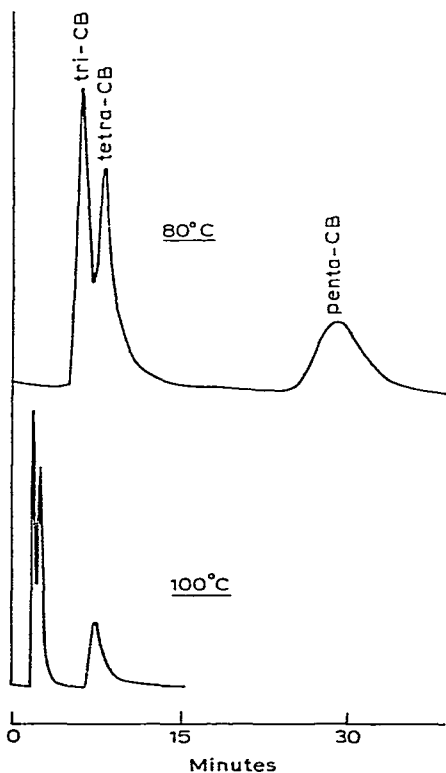

Fig. 2. Chromatograms of 2',3,4-trichlorobiphenyl (tri-CB), 2,2',5,5'-tetrachlorobiphenyl (tetra-CB) and 2,2',4,5,5'-pentachlorobiphenyl (penta-CB) on a 1-m Apolane-87 capillary column at 80 and 100°C.

shows that the resolution of the column was sufficient to allow several compounds to be chromatographed at once. The use of a longer column would have been inconvenient because of the extremely long retention times for compounds of low vapor pressure at low column temperatures. On the 1-m column, 40 min were required to elute 2,4,5-TIB at 70°C and 3 ml/min carrier gas flow-rate, while 1100 min were required to elute the same compound from Hamilton's 0.6-m packed column at 72°C and a carrier gas flow-rate of 66 ml/min[4]. On the 1-m WCOT column, 175 min were required to elute 2,2′,4,5,5′-pentachlorobiphenyl at 60°C.

Table III shows a comparison between vapor pressures determined by this method and those measured by us using gas saturation[9], along with literature values where available[3,10].

TABLE III

COMPARISON OF VAPOR PRESSURES DETERMINED BY GAS CHROMATOGRAPHY AND GAS SATURATION TECHNIQUES

Compound	Temperature (°C)	p^0 (Torr)		Literature
		Gas chromatography	Gas saturation[9]	
Pesticides				
p,p′-DDT	30	$14.0 \cdot 10^{-6}$	$13.0 \cdot 10^{-6}$	$6.5 \cdot 10^{-6}$ (ref. 10)
o,p′-DDT	30	$8.4 \cdot 10^{-6}$	$8.8 \cdot 10^{-6}$	$5.5 \cdot 10^{-6}$ (ref. 10)
2,4,5-T, n-butyl ester	25	$1.6 \cdot 10^{-5}$	—	$1.5 \cdot 10^{-5}$ (ref. 3)
PCB isomers				
2′,3,4-TCB	25	$8.0 \cdot 10^{-5}$	$10.0 \cdot 10^{-5}$	—
2,2′,5,5′-TCB	25	$5.5 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	—
2,2′,4,5,5′-PCB	25	$9.2 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$	—

CONCLUSIONS

Capillary gas chromatography is a rapid and convenient means of determining vapor pressures. The solid PCB isomers 2′,3,4-trichlorobiphenyl and 2,2′,5,5′-tetrachlorobiphenyl are major components of the commercial fluid Aroclor® 1242 which has a reported vapor pressure of $4.1 \cdot 10^{-4}$ Torr, and 2,2′,4,5,5′-pentachlorobiphenyl is a major component of Aroclor® 1254 which has a reported vapor pressure of $7.7 \cdot 10^{-5}$ Torr[2]. The vapor pressures determined for the solid individual PCB isomers are approximately 5–10 times lower than those reported for the liquid commercial mixtures. Vapor pressures determined by gas chromatography agreed well with those determined by gas saturation.

ACKNOWLEDGEMENTS

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