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GAS CHROMATOGRAPHIC MEASUREMENT OF VOLATILITY OF HERBICIDE ESTERS

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SUMMARY

The vapour pressures of eleven herbicide esters were calculated from gas chromatographic measurement of relative retention volumes (dibutyl phthalate = 1) on a non-polar SE-30 column. Measurements were made at temperatures from 72 to 182°C, but by assuming that the ratio of the latent heat of vaporization of the ester to that of dibutyl phthalate was independent of temperature, values for vapour pressure could be extrapolated to 25°C. Vapour pressures at 25°C ranged from $2.5 \cdot 10^{-4}$ mmHg for 2,4-D ethyl ester to $1.9 \cdot 10^{-7}$ mmHg for picloram isooctyl ester.

INTRODUCTION

Volatile esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) have caused concern because of their tendency to vaporize and drift to non-target crops. When the esters are in the vapour form there is no operator control over which area receives the herbicides; this will depend on the vagaries of winds and air currents. Such herbicide drift has caused considerable crop damage on occasion and must be avoided where possible. When a herbicide is to be used in the vicinity of susceptible crops its official registration for such use will depend, among other things, on its low volatility.

In order to put volatility considerations on a quantitative basis it was decided that the vapour pressures of the herbicide esters registered in Queensland should be found. A literature search revealed that only three of the eleven herbicide esters registered for use had recorded vapour pressures. It thus became necessary to make vapour pressure measurements.

Possible ways of measuring vapour pressures include vacuum distillation, differential thermal analysis, effusion, gas saturation and gas-liquid chromatography. Because of familiarity with gas chromatography (GC) and its ready availability this technique was chosen. An added advantage was the tolerance of GC to relatively impure compounds. Jensen and Schall¹ extrapolated the results to vapour pressure values at 25°C after making GC measurements on 2,4-D and 2,4,5-T esters at higher temperatures.

This paper reports an adaptation of the method of Jensen and Schall¹ using a modified theory for extrapolation to 25°C.

EXPERIMENTAL

Esters

The following esters were prepared by esterifying the acid with the alcohol using sulphuric acid as catalyst; 2,4-D ethyl, 2,4-D butoxyethyl, MCPA butoxyethyl, fenoprop *n*-butyl, 2,4,5-T *n*-butyl, 2,4,5-T isobutyl, 2,4,5-T butoxyethyl and 2,4,5-T 2-ethylhexyl.

Chlorthal dimethyl was crystallised from a commercial product, Dacthal W75. Picloram isooctyl and 2,4,5-T isooctyl were isolated, by column chromatography, from a commercial product Dow Tordon 255. Dibutyl phthalate was reagent grade.

Gas chromatography

The gas chromatograph was a Hewlett-Packard 5830 with a flame-ionisation detector. The column was stainless steel, 0.6 m × 3.2 mm O.D. packed with 10% SE-30 on acid-washed, silanised Embacel (60–100 mesh) and was conditioned at 275°C. Gas flow-rates were: 66 ml/min for nitrogen carrier; 192 ml/min (temperature < 100°C) and 238 ml/min (temperature > 100°C) for air; 52 ml/min for hydrogen. The detector and injector were operated at 20–50°C above column temperature.

Retention times less than approximately 100 min were recorded by the computing gas chromatograph while longer times were measured by the distance along the chart. Under the operating conditions the retention time of the solvent was 2–3 sec (equivalent to the "air peak") which could be ignored, so the corrected retention time was taken to be the same as the measured retention time.

A number of the compounds had retention times too close to allow adequate resolution. Appropriate mixtures of the esters dissolved in acetone were prepared, which allowed retention time measurements on the minimum of injections.

GC measurements were made on the esters down to temperatures where their retention times were of the order of 1000 min.

THEORY

Jensen and Schall¹ give the relation between retention volumes (V_R) and vapour pressures (p^0) for two substances run on a column under the same conditions. When z is the chart distance between air and solute peaks

$$V_{R1}/V_{R2} = z_1/z_2$$

For a non-selective column (e.g. silicone SE-30) Jensen and Schall¹ state the relation

$$z_1/z_2 = p_1^0/p_2^0$$

This equation is a mistake which has been repeated by Plimmer² and should be

$$z_1/z_2 = p_2^0/p_1^0$$

because the substance with the higher vapour pressure will elute first.

It then follows that

$$V_{R1}/V_{R2} = p_2^0/p_1^0 \quad (1)$$

Othmer³ has described a method for correlating vapour pressure and latent heat data starting with the Clapeyron–Clausius equation for vaporization of a liquid

$$\frac{dp^0}{dT} = \frac{L}{(V - v)T}$$

where T = absolute temperature, L = latent heat per mole, V = vapour volume per mole, and v = liquid volume per mole.

Assuming that the perfect gas law is followed and that v is insignificant compared with V ,

$$\text{then } \frac{dp^0}{dT} = \frac{Lp^0}{RT^2}$$

$$\text{i.e. } 1/L \, d \ln p^0 = 1/RT^2 \, dT \quad (2)$$

The limitations of eqn. 2 depend on the range of temperature and pressure over which L may be regarded as constant. This equation cannot be solved where L is an unknown function of p^0 or T .

Eqn. 2 may be written for two substances at the same temperature,

$$1/L_1 \, d \ln p_1^0 = 1/RT^2 \, dT$$

$$1/L_2 \, d \ln p_2^0 = 1/RT^2 \, dT$$

$$\text{i.e. } d \ln p_1^0 = L_1/L_2 \, d \ln p_2^0 \quad (3)$$

Othmer³ has shown that eqn. 3 is more useful over a wider temperature and pressure range than eqn. 2 and states that the term L_1/L_2 will be substantially unchanged (especially for related compounds) over a much wider range than either L_1 or L_2 , since the variation of both will follow the same law, and the quotient will be comparatively unchanged.

Integrating eqn. 3 gives

$$\ln p_1^0 = L_1/L_2 \ln p_2^0 + C \quad (4)$$

where C is a constant of integration

Taking logarithms of eqn. 1 gives

$$\ln p_1^0 = \ln p_2^0 - \ln (V_{R1}/V_{R2}) \quad (5)$$

From eqns. 4 and 5 we obtain

$$\ln p_2^0 - \ln (V_{R1}/V_{R2}) = L_1/L_2 \ln p_2^0 + C$$

$$\text{i.e. } \ln (V_{R1}/V_{R2}) = (1 - L_1/L_2) \ln p_2^0 - C \quad (6)$$

A plot of $\ln (V_{R1}/V_{R2})$ vs. $\ln p_2$ should give a straight line with slope $1 - L_1/L_2$ and intercept $-C$, where V_{R1}/V_{R2} is the relative retention volume at the temperature where the reference compound has vapour pressure p_2^0 .

The vapour pressure of component 1 at 25°C, $(p_1^0)_{25}$ may then be calculated from the known vapour pressure, $(p_2^0)_{25}$ of the reference compound at 25°C, and the constants of the above linear equation.

From eqns. 1 and 6 we obtain

$$\ln (p_2^0)_{25} - \ln (p_1^0)_{25} = (1 - L_1/L_2) \ln (p_2^0)_{25} - C$$

$$\text{i.e. } \ln (p_1^0)_{25} = (L_1/L_2) \ln (p_2^0)_{25} + C \quad (7)$$

RESULTS

The retention volumes were calculated by multiplying the measured retention times by the carrier flow-rate (66 ml/min). Table I shows the retention volumes of dibutyl phthalate (V_R) and relative retention volumes (dibutyl phthalate = 1) of the other esters.

The vapour pressure of dibutyl phthalate at each temperature was calculated from the equation of Small *et al.*⁴

Regression lines were fitted to the data according to eqn. 6. The constants for these lines are shown in Table II, which also includes the vapour pressure for each ester at 25°C calculated using eqn. 7, taking the vapour pressure of dibutyl phthalate at 25°C to be $2.0 \cdot 10^{-5}$ mm.

DISCUSSION

The coating of the support material of the column was at a relatively high level (10% SE-30); this was to minimise adsorption effects and ensure that the chromatographic process was exclusively partition. Berezkin⁵, in a review of adsorption in gas-liquid chromatography says that tailing peaks are indicative of residual adsorption of the polar dissolved compound (alcohol, ketone, ester) on the support. On the SE-30 column used here the ester peaks were of good symmetry. This is circumstantial evidence that adsorption was minor compared with partition.

Non-polar columns have been used in a number of applications involving boiling point and vapour pressure determinations. Green *et al.*⁶ used SE-30 to simulate distillation of hydrocarbons. Martin and co-workers used SE-30 to calculate the boiling points of a series of phenothiazines⁷ and treated retention times as a function of boiling points for identification of barbiturates⁸. Castello and D'Amato^{9,10} measured vapour pressures of C₆-C₉ alkanes on a column of SF-96. They found some variation in activity coefficient (reflecting solute-solvent interaction), which was correlated with molecular structure. Soják *et al.*¹¹ related boiling points and retention indices of hydrocarbons on a squalane column and concluded that changes in structure can cause small changes in activity coefficients. These workers have shown that even non-polar phases may have some selectivity and may not separate exclusively on vapour pressure. The assumptions that selectivity of the SE-30 column was minor and that separation was purely on a vapour pressure basis were not tested by any of the experiments in this work.

TABLE II

VAPOUR PRESSURES OF HERBICIDE ESTERS

Values for the constants in linear eqn. 6, $\ln V_{R1}/V_{R2} = (1 - L_1/L_2) \ln p^\circ - C$, and calculated values for the vapour pressures at 25°C using eqn. 7.

Ester	$(1 - L_1/L_2)$	$-C$	p° 25°C (mmHg)
2,4-D ethyl	0.1224	-1.1974	$2.5 \cdot 10^{-4}$
2,4,5-T isobutyl	0.0156	0.0747	$2.2 \cdot 10^{-5}$
Fenoprop <i>n</i> -butyl	0.0204	0.0872	$2.3 \cdot 10^{-5}$
Chlorthal dimethyl	0.0261	0.1146	$2.4 \cdot 10^{-5}$
2,4,5-T <i>n</i> -butyl	0.0001	0.2570	$1.5 \cdot 10^{-5}$
MCPA butoxyethyl	-0.0366	0.5265	$8.0 \cdot 10^{-6}$
2,4-D butoxyethyl	-0.0604	0.8101	$4.6 \cdot 10^{-6}$
2,4,5-T butoxyethyl	-0.1076	1.3988	$1.5 \cdot 10^{-6}$
2,4,5-T 2-ethylhexyl	-0.1142	1.5964	$1.2 \cdot 10^{-6}$
2,4,5-T isooctyl (1)	-0.1112	1.5798	$1.2 \cdot 10^{-6}$
2,4,5-T isooctyl (2)	-0.1243	1.7535	$9.0 \cdot 10^{-7}$
Picloram isooctyl (1)	-0.1798	2.2500	$3.0 \cdot 10^{-7}$
Picloram isooctyl (2)	-0.2002	2.4947	$1.9 \cdot 10^{-7}$

The calculated vapour pressures of 2,4,5-T *n*-butyl, etc., which have melting points higher than 25°C, will be for the liquid at 25°C, not the solid at 25°C. This is because the figures are obtained from liquid \rightleftharpoons vapour phase changes, not solid \rightleftharpoons vapour changes. In application of the figures, it is the liquid \rightleftharpoons vapour change that is required, because the esters will usually be in solution.

Vapour pressure of dibutyl phthalate

The method is a comparative one, vapour pressures of the esters being calculated from that of the standard compound, dibutyl phthalate. It thus becomes important to assess the values quoted in the literature.

Vapour pressure values for dibutyl phthalate calculated from the equations of Hammer and Lydersen¹², Perry and Weber¹³ and Small *et al.*⁴ are recorded in Table III. Burrows¹⁴ measured the vapour pressure of dibutyl phthalate between 125°C and 157°C and graphically extrapolated to 25°C to obtain a value of $1.9 \cdot 10^{-5}$ mmHg. This is the value reported by Kaye and Laby¹⁵.

The equation of Small *et al.*⁴ was chosen to represent the best values. It agrees reasonably well with the values of Perry and Weber¹³ in their region of measurement and the calculated value at 25°C ($2.0 \cdot 10^{-5}$ mm) is quite close to the value ($1.9 \cdot 10^{-5}$ mm) quoted by Burrows¹⁴.

A figure of $2.0 \cdot 10^{-5}$ mm at 25°C was chosen as the vapour pressure of dibutyl phthalate for the purpose of calculation.

Errors of extrapolation

Errors from extrapolating to temperatures much lower than those of measurement can arise from using a non-linear function which is assumed to be linear or from the error in the slope of a linear function.

The data were, in the first instance, treated by the method of Jensen and Schall¹, *i.e.* by assuming $\log p^\circ$ is a linear function of $1/T$. When this was done it was found that the differences between the measured values and the corresponding values

TABLE III

VAPOUR PRESSURE OF DIBUTYL PHTHALATE

Vapour pressures of dibutyl phthalate were calculated from the formula quoted in each reference. The values shown in brackets are in the region of measurement while all other values are extrapolations.

t ($^{\circ}\text{C}$)	T ($^{\circ}\text{K}$)	Vapour pressure (mmHg)		
		<i>Hammer and Lydersen</i> ^{12*}	<i>Perry and Weber</i> ^{13**}	<i>Small et al.</i> ^{4***}
182	455	(5.485)	6.306	(5.726)
162	435	(2.041)	2.239	(2.191)
144	417	(0.748)	0.810	(0.832)
127	400	(0.258)	0.285	0.300
112	385	0.0903	0.105	0.110
97	370	0.0280	(0.0357)	0.0364
84	357 ^e	$9.07 \cdot 10^{-3}$	(0.0130)	0.0126
72	345	$2.88 \cdot 10^{-3}$	$(4.80 \cdot 10^{-3})$	$4.31 \cdot 10^{-3}$
25	298	$8.68 \cdot 10^{-6}$	$4.44 \cdot 10^{-5}$	$2.03 \cdot 10^{-5}$

$$* \log p^{\circ} = 6.439 - 1011/T - 720000/T^2.$$

$$** \log p^{\circ} = -4450/T + 10.58.$$

$$*** \log p^{\circ} = 7.065 - 1666/T - 547700/T^2.$$

given by the line of best fit gave a curve when plotted against $1/T$. This was the case for each of the esters and showed that the assumptions of the integrated Clapeyron-Clausius equation were not valid for such a wide temperature range.

When eqn. 6 was applied to the data there was no obvious curvature when differences were treated in the same way.

The error arising from the uncertainty of the slope of the line has been minimised by making measurements to as low a temperature as possible (down to 72°C for some compounds). The gas chromatographic column was prepared with this in mind; it was kept short (0.6 m) and a high flow-rate was used (66 ml/min) to minimise retention times.

Comparison with literature values

Comparison of the vapour pressures of the three esters reported in the literature is shown in Table IV.

The differences probably result from Jensen and Schall's¹ implicit assumption of a constant latent heat of vaporization.

TABLE IV

VAPOUR PRESSURES—LITERATURE COMPARISON

Ester	Vapour pressure (mmHg) at 25°C	
	<i>Jensen and Schall</i> ¹	<i>This report</i>
2,4-D ethyl	$1.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$
2,4,5-T α -butyl	$5.2 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$
2,4,5-T 2-ethylhexyl	$1.2 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$

The latent heat of vaporization of dibutyl phthalate can be calculated from the equation of Small *et al.*⁴

$$\log p^0 = 7.065 - 1666/T - 547700/T^2$$

$$\text{i.e. } \ln p^0 = 16.268 - 3836/T - 1.261 \cdot 10^6/T^2$$

$$\frac{d \ln p^0}{dT} = 3836 T^{-2} + 2.522 \cdot 10^6 T^{-3}$$

$$RT^2 \frac{d \ln p^0}{dT} = R(3836 + 2.522 \cdot 10^6 T^{-1})$$

From eqn. 2

$$L = RT^2 \frac{d \ln p^0}{dT}$$

$$\text{i.e. } L = R(3836 + 2.522 \cdot 10^6 T^{-1})$$

Values of L calculated from this relation are shown in Table V. Jensen and Schall² made most of their measurements above 170°C where the latent heat of vaporization is very different from that at 25°C.

From the theory it is expected that the latent heat values for the herbicide esters would vary in a similar way to those of dibutyl phthalate.

TABLE V

LATENT HEAT OF VAPORIZATION OF DIBUTYL PHTHALATE

The latent heat of vaporization (kcal/mole) has been calculated from the relation $L = R(3836 + 2.522 \cdot 10^6 T^{-1})$.

t (°C)	T (°K)	L (kcal/mole)
25	298	24.4
100	373	21.0
150	423	19.4
200	473	18.2

Isooctyl esters

The isooctyl esters of both 2,4,5-T and picloram each gave two peaks on the gas chromatogram. The Merck Index¹⁶ describes isooctyl alcohol as a mixture of closely related isomeric branched-chain primary alcohols, RCH_2OH where R represents a branched heptyl radical, the branch consisting mostly of methyl groups in the 3-, 4- or 5-positions. Austin¹⁷ lists the components of a typical "isooctyl" alcohol mixture as 3,4-dimethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 4,5-dimethyl-1-hexanol, 3-methyl-1-heptanol, 5-methyl-1-heptanol and other unidentified alcohols.

The isooctyl esters were hydrolysed, the mixed isooctyl alcohols isolated and an unsuccessful attempt at identification was made. Capillary GC showed that at least five components were present. No positive identifications were made, and the isooctyl esters of 2,4,5-T and picloram, which each gave two distinct peaks on the SE-30 column have two vapour pressures listed.

CONCLUSIONS

The described method, which is an adaptation of that of Jensen and Schall¹, is a convenient way of measuring vapour pressures. Using different assumptions errors of extrapolation have been reduced.

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