

## CHROMATOGRAPHIC STUDIES OF SILICON COMPOUNDS

I. USE OF A FLAME IONISATION GAUGE IN  
DETERMINATION OF RETENTION DATA

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## INTRODUCTION

As part of a project involving accurate retention data measurements for volatile organo-silicon compounds, and the gas chromatographic study of their reactions, the possibility of using a flame ionisation detector with associated high sensitivity has been studied.

Flame ionisation detectors of various design<sup>1,2</sup> have been described, their theoretical operation has been discussed<sup>3</sup>, but little reference to the detection of either  $\pi$  or  $\sigma$ -bonded organo-metallic compounds has been made.

In this work the detector employed was similar in design to that described by the Associated Octel Co.<sup>4</sup>, and appropriate experimental conditions enabled specific retention data<sup>5</sup> to be obtained for series of Group IV alkyls, hydrocarbons and chloro compounds.

## EXPERIMENTAL

*Detector* (see Fig. 1)

The column consisted of 6 ft. copper U-tubing of  $\frac{1}{4}$  in. O.D., set vertically in a vapour jacket. Samples were injected by means of Hamilton  $\mu$ l syringes or 1 ml gas-tight syringes into a T joint compression fitting at the column inlet. The detector flame chamber was mounted horizontally at the end of the column, on a brass plate (6 cm<sup>2</sup>) over which a screw cover could be fitted. Through the centre of the bottom of the plate was silver-soldered a compression fitting into which the end of the column passed. A piece of glass tubing (3 mm O.D.), with its top 5 mm conically ground, over which a Record hypodermic needle could be fitted, was sealed into this fitting to give insulation from chamber and column. A size 16 needle was cut square to form the jet for the flame. The burner tip was located between two 4 mm<sup>2</sup> platinum electrodes placed parallel, and 5 mm apart (found to give optimum sensitivity), supported on K.L.G. type lead-through insulators soldered into the chamber base. B.O.C. white spot N<sub>2</sub> carrier gas was used, high purity H<sub>2</sub> passed in below the plate (at about 30 ml/min controlled through a needle valve by a capillary manometer), and air for combustion entered the chamber radially at the rate of approximately 400 ml/min, air turbulence being minimised by a  $\frac{1}{2}$  in. layer of glass beads in the chamber base.

The ionisation current passing through the flame under the influence of a polarising potential of 70 V was fed via an amplifier to a potentiometric recorder.

The amplifier used<sup>6</sup> was of a simple impedance matching type, having a sensitivity control giving full-scale deflections of 10 mV for ionisation currents in the range  $10^{-6}$ – $10^{-9}$  A. Care was necessary in earthing of the electrode leads and also amplifier casing as inadequate earthing (resistance less than 100 M $\Omega$ ) could cut out signals completely.

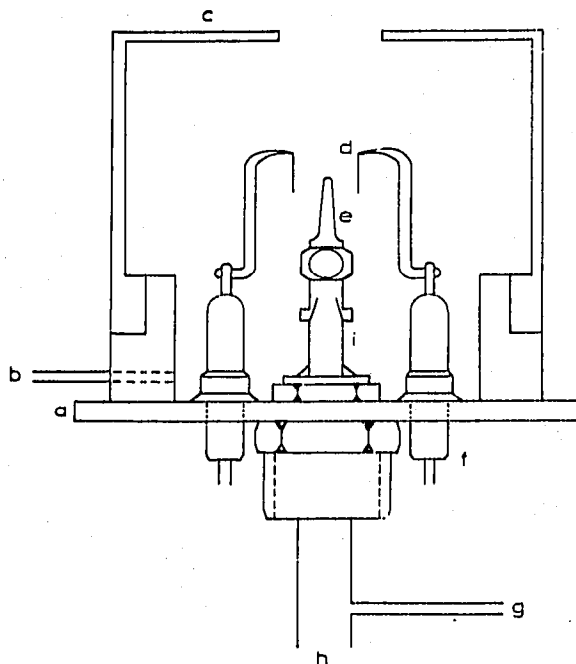


Fig. 1. Flame ionization gauge detector: a = brass-base plate; b =  $\frac{1}{8}$  in. O.D. copper tube for compressed airflow; c = brass cover plate; d = platinum electrode plates; e = jet (No. 16 hypodermic needle); f = ceramic lead-tough connectors; g = hydrogen line; h = nitrogen from column; i = glass tubing.

#### *Chromatography of Group IV alkyls*

For all liquid samples (even samples of a fraction of 1  $\mu$ l) saturation of some kind occurred in the detector, as soon as the ionisation current exceeded approximately  $5 \cdot 10^{-5}$  mA. The type of trace found is seen in Fig. 2 for samples  $\text{Me}_3\text{CEt}$ ,  $\text{Me}_3\text{CCl}$ , and  $\text{Me}_3\text{SiEt}$ ; the flat cut off for the silicon compound being noted. No sensitivity change could remove this fault which was assumed to be due to actual ionisation characteristics in the flame. The assumption of the absence of an actual coating on the electrodes being responsible for this saturation seems justified, since organic compounds chromatographed immediately afterwards showed no change in response.

This difficulty can be overcome by two methods involving decrease in sample size: (1) injection of small samples as vapour in conjunction with the use of the detector at maximum sensitivity, and (2) employment of a bleed-off valve (stream-splitter) between injection seal and column. The data given were obtained by the former method, although the latter has also been used in similar work. Vapour samples taken from above the liquid surface at room temperature gave normal symmetrical peaks giving consistent retention data through the various series. The sizes of vapour/air samples required depended obviously on the vapour pressures of the compounds, but 1  $\mu$ l to 1 ml sample ranges for 26° to 200° (containing in the order of  $10^{-10}$  g) gave ionization currents of  $10^{-8}$ – $10^{-9}$  A, *i.e.* below the saturation limit.

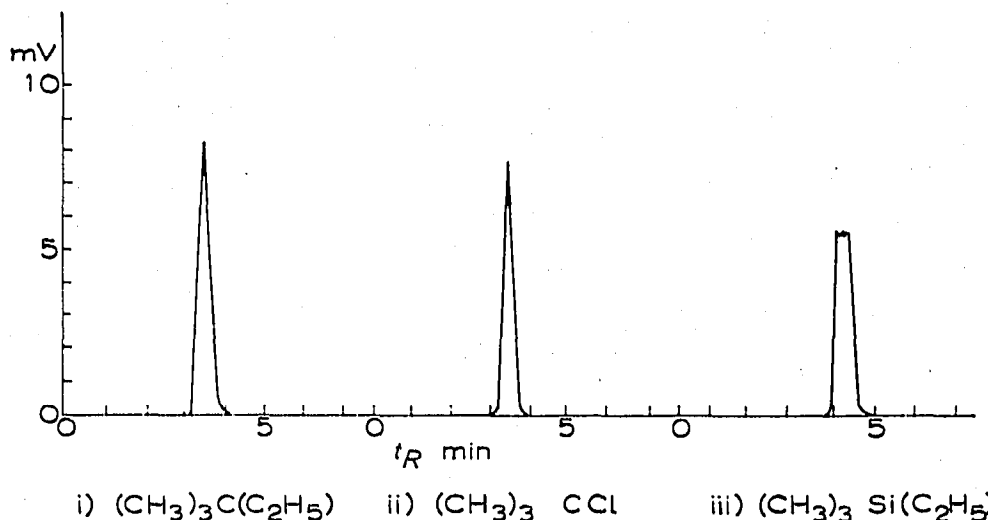


Fig. 2. Chromatographic characteristics for analogous carbon and silicon compounds. Stationary phase: 15% E 301 silicone oil, 80°; carrier gas: nitrogen; flow rate 24.7 ml/min; 1  $\mu$ l liquid sample; F.S.D.  $\approx 10^{-7}$  A.

#### Preparation of alkyl silanes

These were prepared by Grignard reactions of the appropriate alkyl halide with chlorosilanes in di-ethyl ether or di-*n*-butyl ether, having 20% excess of Grignard reagent, followed by fractionating employing purity checking by GLC. Purity was estimated in all cases as  $> 98\%$ .

The course of the fractional distillation of the multi-component system which is always encountered in Grignard reactions of this type, is commonly followed by noting the changes in boiling point and refractive index changes. Such techniques are not completely reliable in such cases in which the boiling points are very close or the differences in refractive indices are small. Often recourse can be made to changes in the infra-red spectra of the fractions, but reliable data on the mixed tetraalkylsilanes are not available. Gas chromatography offers an important and indispensable tool for following fractional distillations of such  $\sigma$ -bonded organo-metallic compounds. Analysis of each fraction as the distillation proceeds, enables a more judicious choice (to be made) in effecting the best separation of components, and therefore affords a maximum amount of each component.

Fig. 3 gives an example of the use of gas chromatography in the isolation and purification of trimethylethylsilane.

(a) *Fractionation*. See the following scheme.

No.	Attenuation	Boiling point range ( $^{\circ}$ C)	Components
1	50	$\rightarrow 35$	I, II, IV
2	50	35-58	I, II, III, IV
3	50	56-60	I, II, III, IV
4	100	57-63	-, II, III, IV
5	100	63	- - III, IV
6	100	63-65	- - III, IV
7	100	63-67	- - III, IV
8	100	Residue	- - IV, V

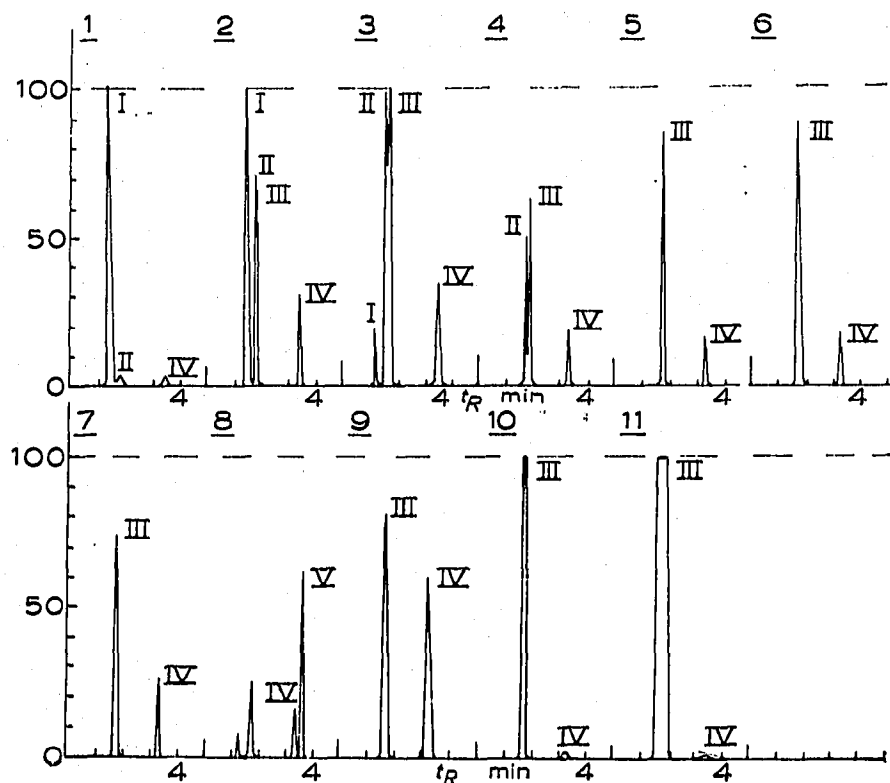


Fig. 3. Gas-liquid chromatography analysis in the preparation of  $(\text{CH}_3)_3\text{SiC}_2\text{H}_5$ . Column: 2 m of 15% E 301 silicone oil on 36-60 celite (treated),  $80^\circ$ ; detector: gas density balance; carrier gas: nitrogen, flow rate 35 ml/min;  $4 \mu\text{l}$  samples injected. I = diethyl ether; II = trimethylchlorosilane; III = trimethylethylsilane; IV = hexamethyldisiloxane.

(b) *Purification.* The fractions containing yields of III were hydrolysed with water to convert III to IV.

9	(originally fraction 3)	100	—	III, IV
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Finally, to remove IV, the fractions were shaken with successive portions of concentrated sulphuric acid.

10	(originally fraction 9)	100	—	III, IV
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Fractions 2-7 were subjected to the water followed by acid treatment, and the fractions combined, and redistilled to produce fraction 11.

11		5	$63.5^\circ$	III, IV
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From the detector response, the purity of the  $\text{Me}_3\text{SiEt}$  was taken as at least 99.8%.

#### Preparation of tin alkyls<sup>8</sup>

$\text{SnMe}_4$  and  $\text{SnEt}_4$  were prepared by Grignard reactions from  $\text{SnCl}_4$ , while the intermediate alkyls were prepared by bromination in equivalent proportions to give  $\text{Me}_3\text{SnBr}$ ,  $\text{Me}_2\text{SnBr}_2$  and  $\text{MeSnBr}_3$  followed by the appropriate Grignard reactions and fractional distillation.  $\text{GeMe}_4$  was made similarly.

Chlorosilanes, hexamethyldisiloxane, normal alkanes, lead tetraethyl and chlorinated hydrocarbons were obtained commercially.

## RESULTS

The compounds chromatographed included hydrocarbons and chlorinated compounds to provide some comparison for specific retention data, namely:

SiMe <sub>4</sub>	SnMe <sub>4</sub>	GeMe <sub>4</sub>	Me <sub>3</sub> SiCl	Me <sub>3</sub> CCl	C <sub>6</sub> H <sub>6</sub>
Me <sub>3</sub> SiEt	Me <sub>3</sub> SnEt		Me <sub>2</sub> SiCl <sub>2</sub>	Me <sub>2</sub> CCl <sub>2</sub>	<i>n</i> -C <sub>5</sub> H <sub>12</sub> - <i>n</i> -C <sub>9</sub> H <sub>20</sub>
Me <sub>2</sub> SiEt <sub>2</sub>	Me <sub>2</sub> SnEt <sub>2</sub>		MeSiCl <sub>3</sub>	HCCl <sub>3</sub>	
MeSiEt <sub>3</sub>	MeSnEt <sub>3</sub>		SiCl <sub>4</sub>	CCl <sub>4</sub>	
SiEt <sub>4</sub>	SnEt <sub>4</sub>	PbEt <sub>4</sub>			
Me <sub>3</sub> SiPr- <i>n</i> , Me <sub>3</sub> SiBu- <i>n</i> , Et <sub>3</sub> SiH, Me <sub>3</sub> SiOSiMe <sub>3</sub>					

With the apparatus described as above, consistent results for vapour samples were obtained for all except the chlorosilanes.

Trimethylchlorosilane showed almost complete hydrolysis to hexamethyldisiloxane, while the di- to tetrachloro compounds gave no response. This was assumed to

TABLE I  
SPECIFIC RETENTION VOLUMES  $V_R$  (ml) ON 15% E 301 SILICONE OIL

Compound	80°	100°	110.5°	140°
SiMe <sub>4</sub>	11.82 ± 0.15	7.65 ± 0.07	6.31 ± 0.07	3.09 ± 0.03
Me <sub>3</sub> SiEt	31.4 ± 0.2	18.45 ± 0.06	13.77 ± 0.2	7.51 ± 0.05
Me <sub>2</sub> SiEt <sub>2</sub>	79.2 ± 0.5	43.2 ± 0.2	32.0 ± 0.7	16.4 ± 0.2
MeSiEt <sub>3</sub>	190.9 ± 0.9	98.7 ± 0.7	68.3 ± 1.8	34.1 ± 0.1
SiEt <sub>4</sub>	446.8 ± 2.7	216.8 ± 3.0	147.7 ± 2.9	69.3 ± 0.4
Me <sub>3</sub> SiPr- <i>n</i>	61.6 ± 0.6	34.3 ± 0.4	24.9 ± 0.1	13.33 ± 0.2
Me <sub>3</sub> SiBu- <i>n</i>	129.3 ± 2.0	68.0 ± 0.2	47.7 ± 0.2	24.3 ± 0.1
Et <sub>3</sub> SiH	118.8 ± 0.4	64.6 ± 1.1	44.8 ± 0.6	23.2 ± 0.1
Me <sub>3</sub> SiOSiMe <sub>3</sub>	74.4 ± 0.5	40.1 ± 0.1	28.4 ± 0.4	14.7 ± 0.05
GeMe <sub>4</sub>	20.1 ± 0.05	12.37 ± 0.12	9.29 ± 0.1	—
SnMe <sub>4</sub>	50.1 ± 0.3	28.4 ± 0.1	21.0 ± 0.4	11.2 ± 0.1
Me <sub>3</sub> SnEt	116.6 ± 1.0	62.3 ± 0.3	43.9 ± 0.3	22.5 ± 0.3
Me <sub>2</sub> SnEt <sub>2</sub>	264.3 ± 3.2	131.2 ± 1.0	91.3 ± 1.2	44.0 ± 0.4
MeSnEt <sub>3</sub>	577.0 ± 9.1	270.5 ± 1.8	181.9 ± 0.9	82.7 ± 1.0
SnEt <sub>4</sub>	122.4 ± 10.0	546.4 ± 7.0	355.0 ± 3.3	153.9 ± 2.4
PbEt <sub>4</sub>	—	1171.5 ± 9.0	713.3 ± 3.3	293.1 ± 5.0
Me <sub>3</sub> CCl	23.4 ± 0.3	14.3 ± 0.1	10.81 ± 0.15	5.98 ± 0.03
Me <sub>2</sub> CCl <sub>2</sub>	24.1 ± 0.4	14.8 ± 0.2	11.2 ± 0.25	6.36 ± 0.05
MeCCl <sub>3</sub>	40.6 ± 0.3	24.0 ± 0.2	17.8 ± 0.2	9.93 ± 0.09
HCCl <sub>3</sub>	40.0 ± 0.3	23.5 ± 0.1	17.4 ± 0.3	9.65 ± 0.1
CCl <sub>4</sub>	63.5 ± 0.2	36.2 ± 0.3	26.4 ± 0.5	14.5 ± 0.11
C <sub>6</sub> H <sub>6</sub>	60.6 ± 0.8	34.8 ± 0.05	25.4 ± 0.4	14.2 ± 0.1
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	17.1 ± 0.2	10.76 ± 0.08	8.17 ± 0.15	4.62 ± 0.02
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	38.5 ± 0.2	22.5 ± 0.01	16.8 ± 0.2	8.65 ± 0.05
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	84.8 ± 0.8	46.2 ± 0.04	33.1 ± 0.6	16.9 ± 0.08
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	184.7 ± 1.8	94.2 ± 1.1	65.2 ± 0.8	31.8 ± 0.1
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	400.7 ± 6.9	188.4 ± 2.0	129.1 ± 2.9	58.8 ± 0.7

be due to complete hydrolysis of the vapour and not detector or column characteristics, since these compounds have since been chromatographed with appropriate precautions to minimise hydrolysis both with this detector using the stream splitting system for liquid samples, and also on a katharometer.

Retention data are recorded on 15 % silicone oil E 301, (mol. wt. 700,000) on Celite treated<sup>9</sup> by dry-sieving to mesh 36-60, washing with conc. HCl, methanol, and distilled water, followed by drying at 300°; phases of this type were used in the chromatography of chlorosilanes<sup>10</sup>.

The values of specific retention volumes  $V_g$  given in Table I are the mean values at each temperature of determinations at inlet/outlet pressure ratios of 1.2, 1.4 and 1.6.

Errors given on this mean are in almost all cases less than  $\pm 2\%$ ; this being smaller than that which may be expected from experimental error.

#### DISCUSSION

Vapour samples taken as described are useful in the measurement of accurate specific retention data, since they give an approximation to ideal chromatography, *i.e.* sample size approaching zero, and injection as a plug of vapour. However, for quantitative sensitivity measurement the disadvantages are: (i) uncertainty as to exact quantities, and (ii) diminution of sample size taken for higher boiling compounds.

Among items of interest in the range of compounds detected are: (a) the ability to detect chloro compounds, *e.g.*  $\text{CCl}_4$  with relatively little loss of sensitivity, (b) the response of the detector to silicon compounds of similar boiling point to analogous carbon compounds, is approximately 20 % greater, and (c) evidence for the formation of ions in the flame deriving from the case of lead tetraethyl. Here, after injection of a liquid sample, a red deposit was formed on the negative electrode, thus indicating the formation of positive lead ions in the flame.

#### GRAPHICAL TREATMENT OF RETENTION DATA

A plot (Fig. 4) of  $\log_{10} V_g$  against column temperature for members of the various series shows good straight lines at temperatures of 80°, 100° and 110.6°, but marked discontinuity at 140°. Since the relative displacement is similar for all compounds, and a straight line extrapolation would indicate a column temperature some 8-10° lower than that used, there would seem to be some discontinuity in stationary phase retention characteristics between 110.6° and 140°. (The only exception being in the case of the very small retention volume obtaining for silicon tetramethyl at 140°). This phenomenon which is being further investigated, may be compared with a similar discontinuity observed with Apiezon L between 58° and 80°<sup>11</sup>.

Figs. 5 and 6 show plots of  $\log V_g$  and number of carbon atoms for the silicon and tin tetraalkyls, and also the normal paraffins at column temperatures of 80° and 140° respectively. (The intermediate temperature graphs show parallel characteristics.)

In comparison with the paraffins which show a close approximation to a linear relationship, both mixed methylethyltetraalkyl series show a slight but consistent curvature, giving rather higher  $\log_{10} V_g$  values for the asymmetrical members than

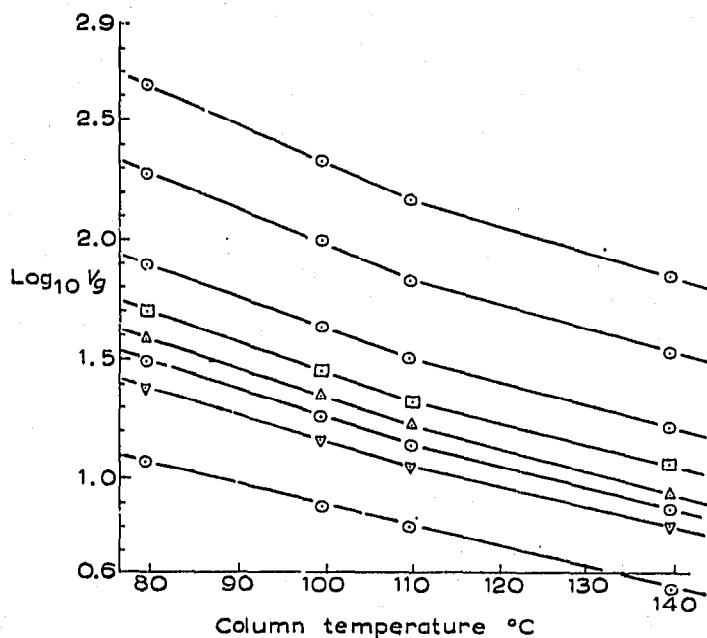


Fig. 4. Plot of  $\log_{10} V_{\theta}$  against column temperature.  $\odot$  = tetraalkylsilanes,  $\text{SiMe}_4$ - $\text{SiEt}_4$ ;  $\square$  = tetramethylstannane;  $\triangle$  = *n*-hexane;  $\nabla$  = *tert.*-butyl chloride.

might be predicted from numbers of carbon atoms only. This indicates some degree of selective retention of the asymmetrical over the symmetrical members, although such an effect should become more pronounced for the mixed methyl-*n*-propyl and methyl-*n*-butyl series at present being investigated. The straight chain trimethylalkyl series, however, appears to show curvature in the opposite direction, perhaps indicating some selective retention as the chain lengthens.

Fig. 7 shows a plot of  $\log_{10} V_{\theta}$  against boiling point giving closely similar plots for

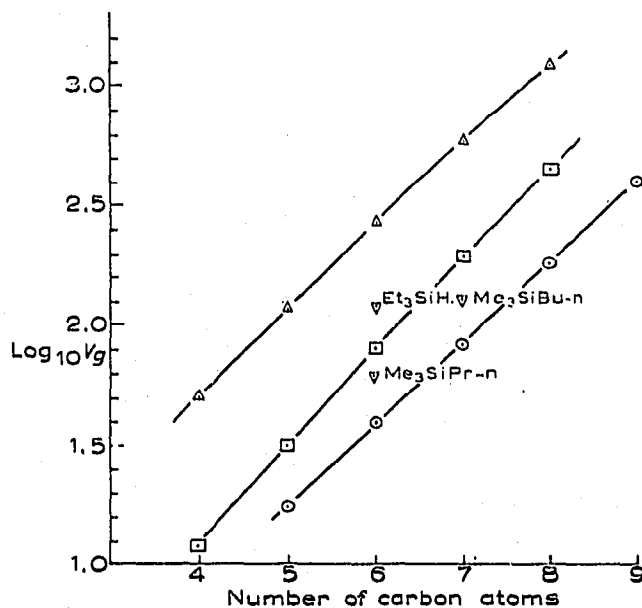


Fig. 5. Plot of  $\log_{10} V_{\theta}$  against number of carbon atoms at  $80^{\circ}$ .  $\square$  = tetraalkylsilanes,  $\text{SiMe}_4$ - $\text{SiEt}_4$ ;  $\triangle$  = tetraalkylstannanes,  $\text{SnMe}_4$ - $\text{SnEt}_4$ ;  $\odot$  = *n*-alkanes.

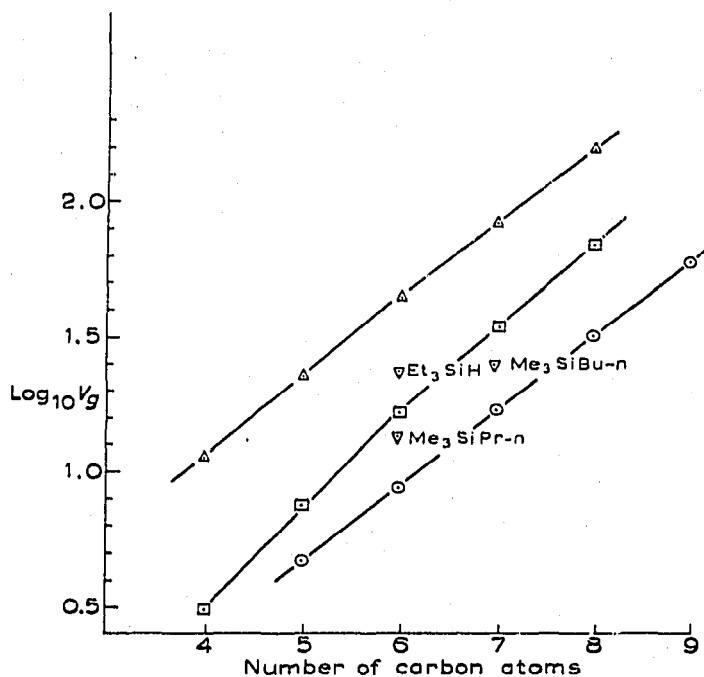


Fig. 6. Plot of  $\log_{10} V_g$  against number of carbon atoms at  $140^\circ$ . ◻ = tetraalkylsilanes; Δ = tetraalkylstannanes; ○ = *n*-alkanes.

the four column temperatures. A general upward curve for each temperature is noted, giving higher retention volumes than predicted for the higher boiling compounds. A number of compounds, however, show some exception to this general trend. Trimethyl-*n*-propyl- and *n*-butylsilanes always appear somewhat below the

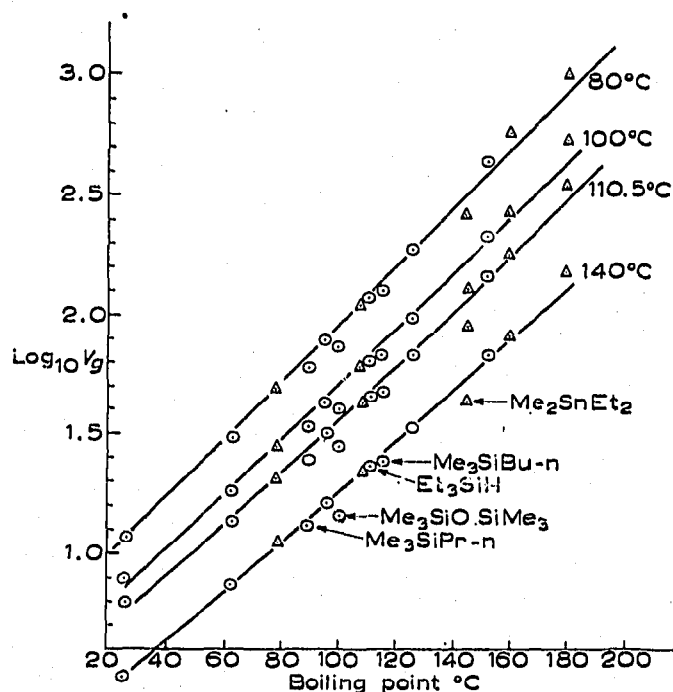


Fig. 7. Plot of  $\log_{10} V_g$  against boiling point for different column temperatures. ○ = tetraalkylsilanes; Δ = tetraalkylstannanes.



curve, but the two major exceptions are hexamethyldisiloxanes which always have a markedly lower retention volume than predicted from its boiling point (this has also been noted on tritolyl phosphate and Apiezon L phases<sup>11</sup>), and dimethyldiethyl tin.

This compound always appears so far below the curve that to place it on the line would mean assigning a boiling point of 138° instead of 144°. This anomalous result warrants further study since the boiling point range of the methylethyl tins, (*i.e.* 78°, 108°, 145°, 159° and 181°) shows successive differences on replacement of methyl by ethyl of 30°, 37°, 14° and 27°, in comparison with a similar series of differences in the analogous silicon series of 37°, 32°, 31° and 26°. It is seen in fact, that a boiling point of 138° assigned to dimethyldiethyl tin would make for a much closer comparison between the series.

#### ACTIVITY COEFFICIENT MEASUREMENTS

HARDY<sup>12</sup> referred to recent papers on the study of the thermodynamics of systems of involatile solvents and volatile solutes by gas chromatography, and indicated the accuracy possible in experiments having the necessary degree of control and measurement of operating parameters.

Generally, for non-polar solutes and solvents, values of activity coefficients at infinite dilution ( $\gamma^{\circ}$ ) are found to be in the range 0.1–1.0 when calculated from the equation:

$$\gamma_p^{\circ} = \frac{N_{11q}RT}{kp_c}$$

where  $k$  is the partition coefficient obtained by dividing  $V^{\circ}_r$  by the volume of the stationary phase at the column temperature,  $V^{\circ}_r$  being here given as the product of the specific retention volume  $V_g$  and the weight of solvent.  $N_{11q}$  is the number of moles of liquid phase per unit volume at temperature  $T^{\circ}\text{K}$ .

Thus:

$$\gamma_p^{\circ} = \frac{W_l \times RT}{M \times V_l} + \frac{V_g \times W_l}{V_l \times p} = \frac{RT}{V_g \times M \times p} \quad (1)$$

where  $p$  = vapour pressure in mm Hg of solute at temperature  $T$ ,

$W_l$  = weight of liquid phase,

$V_l$  = volume of liquid phase,

$M$  = molecular weight of liquid phase.

Thus accurate molecular weights, vapour pressure values and specific retention data are needed for such measurements. Since, however, the molecular weight of E 301 is approximately 700,000, it would seem likely that the  $\gamma_p^{\circ}$  values would be very small. Although, as HARDY states, accurate values cannot be obtained under these conditions, series of relative values for various series of compounds may be calculated. Although it is doubtful whether such values are strictly activity coefficients, they do represent some analogous thermodynamic property of the system and may thus be of some interest.

Thus where possible, these values have been calculated, the limiting factor being the availability of accurate vapour pressure data over the temperature range chromatographed.

Antoine equations of the type:

$$\log_{10} p = A - \frac{B}{(c + t)} \quad (t \text{ in } ^\circ\text{C})$$

are available<sup>13</sup> for the *n*-paraffins, benzene, neohexane, chloroform and carbon tetrachloride, and equations of the type:

$$\log_{10} p = C - \frac{B}{T} \quad (T \text{ in } ^\circ\text{K})$$

for tin tetramethyl and lead tetraethyl.

Tabulated values up to their boiling points<sup>13</sup> are available for trimethylethyl, *n*-propyl- and *n*-butylsilanes, methyltriethylsilane, tetraethylsilane, hexamethyldisiloxane and trimethylethyl tin, which give almost linear plots of  $\log_{10} p$  against  $1/T^\circ\text{K}$  (Fig. 8). Interpolation of the required values of  $1/T^\circ\text{K}$  corresponding to column temperatures, gives appropriate vapour pressure values (assuming linearity to hold

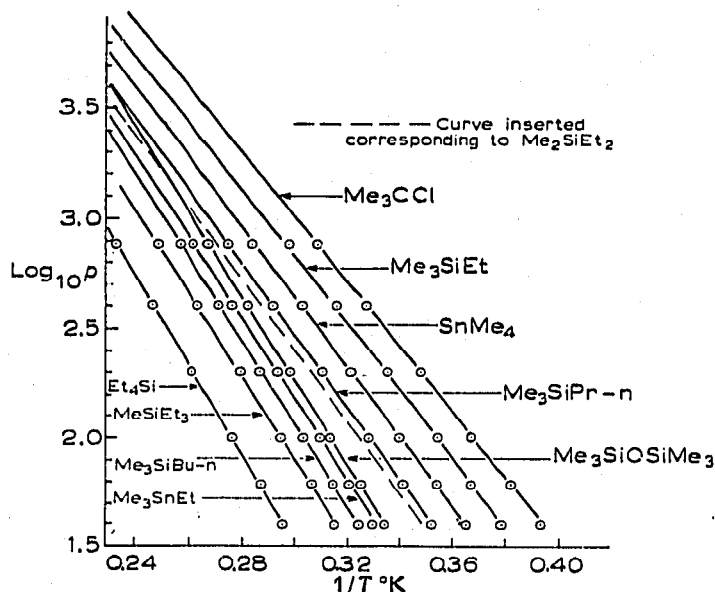


Fig. 8. Vapour pressure curves,  $\log_{10} p$  ( $p$  in mm Hg) against  $1/T^\circ\text{K}$ .

above the boiling point where this applies). Values for dimethyldiethylsilane were estimated by inserting its boiling point in the  $\log_{10} p$  against  $1/T^\circ\text{K}$  plot, and constructing the best plot by comparison with the other members of the methylethylsilane series.

The values calculated from eqn. (1) designated by  $\gamma_N$  are given in Table II.

#### CONCLUSIONS

A number of general points may be made on the values calculated. As anticipated from eqn. (1), and the high molecular weight of the solvent, the values were of the order of  $1/1000$  of those found previously (e.g. for halogenated hydrocarbons on silicone 702, mol. wt. 530<sup>12</sup>). This factor is seen to be of the order of the molec-

TABLE II

VALUES OF  $\gamma_N$  ON 15% E 301 SILICONE OIL, GIVEN TO ONE DECIMAL PLACE  
(SHOWING THE SECOND AS CALCULATED)

Compound	$\gamma_N \times 10^{-4}$			
	80°	100°	110.5°	140°
SiMe <sub>4</sub>	7.6 (1)	7.7 (2)	7.9 (2)	9.2 (3)
Me <sub>3</sub> SiEt	7.7 (7)	8.2 (6)	8.7 (2)	8.8 (3)
Me <sub>2</sub> SiEt <sub>2</sub>	8.4 (9)	9.0 (3)	9.1 (0)	9.5 (7)
MeSiEt <sub>3</sub>	9.5 (1)	9.9 (2)	10.9 (2)	11.2 (9)
SiEt <sub>4</sub>	9.6 (3)	10.1 (3)	10.7 (3)	9.9 (2)
Me <sub>3</sub> SiPr- <i>n</i>	9.0 (8)	9.7 (5)	10.4 (8)	10.7 (7)
Me <sub>3</sub> SiBu- <i>n</i>	9.6 (9)	9.9 (9)	10.6 (0)	10.2 (5)
Me <sub>3</sub> SiOSiMe <sub>3</sub>	10.8 (1)	10.8 (5)	10.9 (8)	10.6 (1)
Me <sub>3</sub> CEt	7.3 (9)	7.8 (6)	8.2 (8)	9.0 (0)
Me <sub>3</sub> CCl	7.1 (0)	7.5 (4)	7.6 (8)	7.8 (3)
HCCl <sub>3</sub>	5.9 (9)	6.3 (1)	6.7 (9)	6.8 (6)
CCl <sub>4</sub>	5.8 (7)	6.2 (2)	6.7 (2)	6.7 (7)
SnMe <sub>4</sub>	7.7 (8)	8.2 (3)	8.6 (8)	9.1 (8)
Me <sub>3</sub> SnEt	8.5 (3)	8.8 (7)	9.4 (6)	9.1 (7)
PbEt <sub>4</sub>	—	7.9 (1)	8.0 (0)	—
C <sub>6</sub> H <sub>6</sub>	6.8 (5)	7.2 (2)	7.5 (4)	7.2 (1)
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	6.6 (7)	6.9 (9)	7.5 (3)	8.0 (2)
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	7.6 (4)	7.9 (4)	8.4 (5)	9.2 (7)
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	8.6 (6)	9.0 (3)	9.6 (3)	9.7 (5)
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	9.7 (2)	10.0 (3)	10.6 (8)	10.4 (1)
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	10.8 (0)	11.1 (8)	11.6 (0)	11.3 (0)

ular weight difference between these two silicone oils. The effect of increase in temperature produces a characteristic increase in  $\gamma_N$  with the exception of the 140° values, which are lower than anticipated. This break in the trend thus follows the discontinuity already noted for the log  $V_g$ -column temperature graph. A fairly regular increase is usually noted with increase in boiling point through a series, although the chlorinated hydrocarbons show lower values than expected from boiling point only. Hexamethyldisiloxane again shows some departure from the general trends, having a relatively higher value of  $\gamma_N$ .

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## SUMMARY

The use of a flame ionisation detector in the chromatography of Group IV alkyls and analogous compounds is described including some discussion of unusual sensitivity characteristics in their chromatography. Specific retention data are calculated and correlated, and thermodynamic quantities similar in type to an activity coefficient at infinite dilution are calculated and discussed.

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