THE COMPILATION AND CORRELATION OF RETENTION DATA FOR ALKYL SILANES, GERMANES, DIGERMANES AND BORAZOLES AND SOME OF THEIR HYDROCARBON ANALOGUES

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Our studies in silicon, germanium and borazole chemistry have led to the preparation of a considerable number of alkyl derivatives of silane, germane, digermane and borazole, the latter both N- and B-substituted. Gas chromatographic retention data for these compounds will be presented in a condensed form in this paper; a large number of these values have not hitherto been published. It is also our object to show how there are patterns between $\log t_R$ values which enable retention times to be predicted. A comparison with analogous hydrocarbon systems is possible in all cases, and many of the carbon analogues have not yet been chromatographically characterised. Some of the rules formulated in this paper should be applicable to these uncharacterised hydrocarbons.

The samples were analysed in columns of 2–13 % squalane (and also on 13 % Carbowax 4000 for some of the borazoles) at 100° using flame ionisation detectors and oxygen-free hydrogen as carrier gas. The solid support was Embacel (May and Baker; 60–100 mesh; acid-washed), it was made inactive by treatment with hexamethyldisilazane[1]. Retention data of all the compounds were expressed as logarithms of their retention times relative to mesitylene ($\log t_R = 2$). Results on different columns agreed to within ± 0.01.

SILICON AND GERMANIUM ALKYLS

The use of retention parameters for the calculation of retention times has been found to work well for silanes, germanes and silico-germanes[2], and also for tetraalkyl derivatives of silicon and germanium[3]. For the estimation of $\log t_R$ values of the latter, the alkyl group retention parameters are obtained by dividing the $\log t_R$ values of symmetrical SiR_4 and GeR_4 compounds by 4 to give:

Me 0.10; Et 0.45; Pr^n 0.69; Bu^n 0.93.

The methyl parameter used here was obtained from $\log t_R$ values of $SiMe_4$ and $GeMe_4$ found by graphical extrapolation from SiR_3Me, GeR_3Me and GeR_2Me_2 results. A value of 0.14 for methyl was used previously[3], this gives a closer overall average agreement between observed and calculated values for tetraalkyl derivatives. The parameters can be used to calculate the $\log t_R$ values of mixed tetraalkylsilanes direct; the same parameters can be used for tetraalkylgermanes when a constant of

0.14 is added to the results, and for CR_4 compounds when a constant of 0.09 is subtracted.

As examples of the use of retention parameters for the calculation of log t_R values, Table I shows some observed and calculated results for germanium allyl derivatives (allyl parameter 0.66 from $Ge(allyl)_4$) and hexaalkyldigermanes (Ge–Ge parameter 0.85 from Ge_2Me_6) none of which have been published previously.

TABLE I

OBSERVED AND CALCULATED log t_R VALUES OF SOME ALLYL AND ALKYL DERIVATIVES OF MONO- AND DI-GERMANE

Compound	log t_R		Compound	log t_R	
	(obs.)	(calc.)		(obs.)	(calc.)
$GeMe_3(allyl)$	1.14	1.10	Ge_2Me_6	(1.45)	(1.45)
$GeMe_2(allyl)_2$	1.69	1.66	Ge_2Me_5Et	1.80	1.80
$GeMe(allyl)_3$	2.25	2.22	$Ge_2Me_4Et_2$	2.15	2.15
$Ge(allyl)_4$	(2.79)	(2.78)	$Ge_2Me_3Et_3$	2.50	2.50
$GeEt_3(allyl)$	2.15	2.15	$Ge_2Me_2Et_4$	2.84	2.85
$GeEt_2(allyl)_2$	2.37	2.36	$Ge_2Me_5Pr^n$	2.05	2.03
$GeEt(allyl)_3$	2.59	2.57	$Ge_2Me_4Pr^n_2$	2.62	2.60
			$Ge_2Me_5(allyl)$	2.03	2.01
			$Ge_2Me_4(allyl)_2$	2.59	2.57

The numerical differences between observed and calculated log t_R values of a number of alkyl derivatives of carbon, silicon and germanium are listed in Table II. For mixed alkyls with only two alkyl radicals present, the results are grouped according to the carbon number difference between the radicals.

The results indicate that the more similar in size the alkyl groups in a mixed derivative, the more accurate is the calculation from the alkyl group parameters. In general, the observed differences from predicted values can be related to the symmetry in the molecule, for the more "unsymmetrical" the molecule the greater is the difference. When the alkyl groups in a mixed derivative differ by one carbon number there is an approximate difference of 0.00, when they differ by two carbon numbers it is +0.04 and three carbon numbers it is about +0.08.

Similar calculations for over fifty mixed trialkyl chlorine, bromine and hydrogen derivatives of silicon and germanium do not show as good an agreement with those observed as with the tetraalkyls, and no obvious relation to symmetry in the molecule can be observed[3]. Some preliminary studies with mixed trialkylphosphines, however, show that their retention behaviour resembles that of the corresponding tetraalkylsilanes and retention parameters can be used.

ALKYLBORAZOLES

Borazole is the inorganic analogue of benzene. The preparation of many of the alkylborazoles, whose retention times are discussed here, is described elsewhere. Their characterisation and identification by means of graphical plots of log t_R values against carbon content has been stressed[4–6].

TABLE II

DIFFERENCES BETWEEN OBSERVED AND CALCULATED $\log t_R$ VALUES OF SOME ALKYL DERIVATIVES
OF CARBON, SILICON AND GERMANIUM

$\Delta C = 1^*$

—0.02	$SiMeEt_3$, $GeMeEt_3$
—0.01	$Ge_2Me_3Et_4$, $GePr^nBu^n_3$
0.00	$GeEt_3Pr^n$, $GePr^n_3Bu^n$, $SiPr^n_3Bu^n$, $CMeEt_3$, CEt_3Pr^n, $GeEt_3(allyl)$, Ge_2Me_5Et, $Ge_2Me_4Et_2$, $Ge_2Me_3Et_3$
+0.01	$SiEt_3Pr^n$, $GeEt_2Pr^n_2$, $SiEtPr^n_3$, $GeEtPr^n_3$, $SiPr^n_2Bu^n_2$, $GePr^n_2Bu^n_2$, $SiPr^nBu^n_3$, $GeEt_2(allyl)_2$
+0.02	$SiEt_2Pr^n_2$, $GeEt(allyl)_3$
+0.03	CMe_3Et_2

$\Delta C = 2$

+0.02	$GeEtBu^n_3$, $Ge_2Me_5Pr^n$, $Ge_2Me_4Pr^n_2$, $Ge_2Me_5(allyl)$, $Ge_2Me_4(allyl)_2$
+0.03	$SiMe_2Pr^n_2$, $GeEt_3Bu^n$, $GeMe_2(allyl)_2$, $GeMe(allyl)_3$
+0.04	$SiMePr^n_3$, $SiEt_3Bu^n$, $SiEt_2Bu^n_2$, $GeMe_3(allyl)$
+0.05	$GeMePr^n_n$, $GeEt_2Bu^n_2$
+0.06	$GeMe_2Pr^n_2$, $SiEtBu_3{}^n$

$\Delta C = 3$

+0.05	$GeMe_3Bu^n$
+0.06	$SiMe_3Bu^n$
+0.08	$SiMe_2Bu^n_2$
+0.10	$SiMeBu^n_3$
+0.11	$GeMe_2Bu^n_2$, $GeMeBu^n_3$

Mixed derivatives with more than two radicals

+0.01	$SiMeEt_2Pr^n$, $GeMeEt_2Pr^n$
+0.02	$GeEt_2Pr^nBu^n$, $SiEtPr^n_2Bu^n$, $GeEtPr^n_2Bu^n$, $GeEtPr^nBu^n_2$
+0.03	$SiEtPr^nBu^n_2$, $SiMeEtPr^n_2$, $GeMeEtPr^n_2$, $SiMe_2EtBu^n$
+0.05	$GeMeEt_2Bu^n$, $GeMe_2EtBu^n$
+0.07	$GeMeEtPr^nBu^n$, $SiMePr^n_2Bu^n$
+0.08	$SiMe_2Pr^nBu^n$, $GeMe_2Pr^nBu^n$, $GeMePr^nBu^n_2$, $SiMeEtBu^n_2$
+0.09	$GeMeEtBu^n_2$
+0.10	$GeMePr^n_2Bu^n$

* ΔC is the carbon number difference between the radicals.

Retention parameters for individual alkyl groups were calculated from the $\log t_R$ values of the symmetrical 1,3,5-derivatives by subtracting the $\log t_R$ of borazole (0.54) and dividing by 3 (Table III). The corresponding values for alkyl groups attached to the benzene ring were found in a similar way ($\log t_R$ of benzene 0.85).

TABLE III

RETENTION PARAMETERS FOR ALKYL GROUPS

	H	Me	Et	Pr^n	Pr^i	Bu^t	Bu^s	Bu^i
Tri-N-alkylborazoles	0.00	0.33	0.50	0.77	0.65	0.85	0.88	0.94
Tri-B-alkylborazoles	0.00	0.32	0.65	0.90	0.77	—	—	—
Trialkylbenzenes	0.00	0.38	0.63	(0.87)*	0.72	(0.95)*	(0.93)*	(1.04)*

* The trialkylbenzene Pr^n, Bu^t, Bu^s and Bu^i parameters were estimated from the tri-N-alkylborazole values.

In general, the retention parameters of B-alkylborazoles are closer to those of alkylbenzenes than to N-alkylborazole values. The difference between values for B- and N-alkylborazoles may be related to the free N–H groups (of polar character) in the former compounds, so that N-substituted values are about 0.13 less than B-substituted values or 0.10 less than the aromatic values. On this basis the methyl group parameters are anomalous, low for B-methyl- and high for N-methyl-borazoles. The high N-methyl value may be related to an effect observed by JAMES AND MARTIN[7], the unusual retardation of the tertiary amine, trimethylamine, in the ethereal column liquid "Lubrol MO". They attributed this retardation to "active" methyl groups of the amine forming hydrogen bridges with oxygen in the ether. This conclusion is supported by the unusually high boiling point of trimethylamine relative to other tertiary amines and alkyl analogues of both boron and carbon (Table IV).

The alkyl group retention parameters may be used to calculate the log t_R values of mixed 1,3,5-trialkyl derivatives. Table V lists the differences between some observed and calculated values.

As with the carbon, silicon and germanium tetraalkyls, the more similar in size the alkyl groups in the mixed derivative the more accurate is the calculation of retention times from the alkyl group parameters. Again, the mixed derivatives generally elute later than is predicted from the retention times of symmetrically derivatives, and the more "unsymmetrical" the molecule the greater is the difference. The average deviation between observed and calculated log t_R values for carbon number differences are as follows: 1 carbon number + 0.01; 2 carbon numbers + 0.07; 3 carbon numbers + 0.15(5); 4 carbon numbers + 0.21.

CHANG AND KARR have published retention data for a large number of aromatic hydrocarbons[8,9]. We applied our method of estimating log t_R values to their results which were measured on columns of 25 % Apiezon L on Firebrick at 150° relative to n-propylbenzene. We used a value of 1.30 for the log t_R of benzene; this was found by graphical extrapolation. Our alkylbenzene retention parameters had to be divided by 1.46 to give the CHANG AND KARR parameters. Table VI shows the differences between observed and calculated log t_R values for CHANG AND KARR's results. Their data give similar deviations to ours, and in keeping with the smaller (higher temperature) parameters the deviations are also somewhat smaller.

Parameters may also be used to calculate boiling points, when similar results are obtained. From 1,3,5-trimethyl- and 1,3,5-triethyl-benzene the boiling point parameters for methyl and ethyl groups are derived as 28.2° and 45.4° respectively. The deviations between observed and calculated boiling points for some 1,3,5-methyl- and ethyl-substituted benzenes are as follows: H_2Me + 2.3°; HMe_2 + 2.5°; Me_2Et + 1.9°; $MeEt_2$ + 1.6°; H_2Et + 10.7°; HEt_2 + 10.2°.

A plot of log t_R against boiling point shows that 10° corresponds to an approximate log t_R difference of 0.13. Thus the boiling point deviations are of greater magnitude than the log t_R deviations. This conclusion is in agreement with the observation that the general linear relation between log t_R and boiling point for alkylbenzenes is not exact. A similar observation has been made for alkylborazoles[4].

The log t_R values of methyl- and ethyl-borazoles, substituted on both boron and nitrogen atoms of the ring were calculated from retention parameters in the same way as the unsymmetrical trialkyl derivatives. Table VII lists the numerical differences in the observed and calculated log t_R values.

TABLE IV

BOILING POINTS OF TERTIARY AMINES AND ALKYL ANALOGUES OF BORON AND CARBON

Compound	B.p. (°C)	Compound	B.p. (°C)	Compound	B.p. (°C)
Me_3B	—21.8	Et_3B	95	Pr^n_3B	156
Me_3CH	—10.2	Et_3CH	93.3	Pr^n_3CH	162
Me_3N	3.5	Et_3N	89.5	Pr^n_3N	156

TABLE V

DIFFERENCES BETWEEN OBSERVED AND CALCULATED $\log t_R$ VALUES OF SOME 1,3,5-TRIALKYL DERIVATIVES OF BENZENE AND BORAZOLE

$\Delta C = 1$*

—0.02	$B\text{-}Et_2Pr^n$
—0.01	$B\text{-}EtPr^n_2$
+0.00	$N\text{-}Pr^iBu^t_2$
+0.01	$N\text{-}H_2Me$, $N\text{-}HMe_2$, $B\text{-}HMe_2$, $N\text{-}Pr^i_2Bu^t$, $B\text{-}Me_2Et$, $B\text{-}MeEt_2$, $B\text{-}Et_2Pr^i$, $B\text{-}EtPr^i_2$
+0.02	Me_2Et-benzene, $MeEt_2$-benzene, $N\text{-}Et_2Pr^i$, $N\text{-}EtPr^i_2$
+0.03	H_2Me-benzene, HMe_2-benzene, $N\text{-}Me_2Et$, $N\text{-}MeEt_2$

$\Delta C = 2$

+0.03	$B\text{-}Me_2Pr^n$, $B\text{-}MePr^n_2$
+0.04	$N\text{-}H_2Et$
+0.05	$N\text{-}Me_2Pr^i$
+0.06	$N\text{-}HEt_2$, $N\text{-}MePr^i_2$
+0.07	$B\text{-}H_2Et$, $B\text{-}HEt_2$, $N\text{-}Et_2Bu^t$
+0.08	$N\text{-}Me_2Pr^i$, $N\text{-}MePr^i_2$
+0.09	$N\text{-}EtBu^t_2$, $MePr^i_2$-benzene
+0.10	Me_2Pr^i-benzene
+0.11	HEt_2-benzene
+0.12	H_2Et-benzene

$\Delta C = 3$

+0.10	$N\text{-}H_2Pr^n$
+0.12	$N\text{-}HPr^n_2$
+0.14	$N\text{-}H_2Pr^i$
+0.15	$N\text{-}HPr^i_2$
+0.16	H_2Pr^n-benzene
+0.17	$N\text{-}MeBu^t_2$
+0.18	$N\text{-}Me_2Bu^t$
+0.22	H_2Pr^i-benzene

$\Delta C = 4$

+0.16	$N\text{-}H_2Bu^t$, $N\text{-}HBu^t_2$
+0.20	H_2Bu^s-benzene
+0.21	$N\text{-}H_2Bu^s$, $N\text{-}HBu^s_2$
+0.22	H_2Bu^t-benzene
+0.25	$N\text{-}HBu^t_2$
+0.30	$N\text{-}H_2Bu^t$

Mixed derivatives with three radicals

+0.02	$B\text{-}MeEtPr^i$
+0.04	$B\text{-}MeEtPr^n$
+0.15	$HMePr^i$-benzene

* ΔC is the carbon number difference between the radicals.

TABLE VI

DIFFERENCES BETWEEN OBSERVED AND CALCULATED log t_R VALUES OF SOME 1,3,5-DERIVATIVES OF BENZENE BASED ON SOME RESULTS OF CHANG AND KARR[8]

$\Delta C = 1$*

.. 0.00	H_2Me-benzene
+0.01	HMe_2-benzene, Me_2Et-benzene, $McEt_2$-benzene

$\Delta C = 2$

+0.05	HEt_2-benzene
+0.06	H_2Et-benzene

$\Delta C = 3$

+0.10	H_2Pr^n-benzene
+0.13	H_2Pr^i-benzene

$\Delta C = 4$

+0.13	H_2Bu^i-benzene
+0.16	H_2Bu^s-benzene

Mixed derivatives with different groups 1,3,5

+0.04	HMcEt-benzene
+0.07	$HMePr^n$-benzene
+0.09	$HMePr^i$-benzene

* ΔC is the carbon number difference between the radicals.

It can be seen that alkyl groups on adjacent atoms make retention times of these borazoles very different from those calculated from the simple alkyl group parameters. Thus hexaethylborazole has a retention time less than half that calculated, and hexamethylborazole a retention time twice that calculated. However, an underlying pattern is again apparent, indicating perhaps once again that alkyl groups attached to the borazole ring are affecting the retention times in a regular manner.

Similar calculations of the log t_R values of methylbenzenes measured by CHANG AND KARR give positive deviations of the same order of magnitude as found for methyl-borazoles (Table VIII); these deviations are again reflected in boiling point values.

The corresponding data for ethylbenzenes are not available, but a comparison with the ethylborazoles indicates that *negative* deviations might be expected for tetra-, penta- and hexa-ethyl-benzenes.

TABLE VII

DIFFERENCES BETWEEN OBSERVED AND CALCULATED log t_R VALUES OF METHYL- AND ETHYL-BORAZOLES

	$B\text{-}Me_3$	$B\text{-}Me_2$	$B\text{-}Me$	$B\text{-}Et$	$B\text{-}Et_2$	$B\text{-}Et_3$
N-Me$_3$	+0.30	+0.21	+0.11	+0.05	+0.05	+0.02
N-Me$_2$	+0.18	—	—	—	+0.03	+0.04
N-Me	+0.08	—	—	—	—	+0.01
N-Et	+0.07	—	—	+0.10	+0.05	—0.03
N-Et$_2$	+0.10	+0.05	+0.07	+0.08	—0.04	—0.12
N-Et$_3$	+0.13	+0.07	+0.03	—0.07	—0.19	—0.35

TABLE VIII

DIFFERENCES BETWEEN OBSERVED AND CALCULATED log t_R VALUES AND BOILING POINTS OF METHYL-BENZENES

	1,2,3,5-Tetramethylbenzene	Pentamethylbenzene	Hexamethylbenzene
log t_R, observed—calculated value	+0.12	+0.25	—
Boiling point, observed—calculated value (°C)	+3.1	+9.8	+14.7

The effect of alkyl groups on the retention times of tri-B-alkylborazoles on Carbowax 4000

The specific retardations of borazoles with free N–H groups on Carbowax 4000 have been discussed in the case of N-alkylborazoles[4], methylborazoles[5] and ethylborazoles[6]. It was suggested that hydrogen bonding occurred between N–H groups and oxygen atoms in the column liquid, and that "steric effects" of B-alkyl groups might influence the retardations of borazoles with free N–H groups. Such effects would correspond to those observed in the case of alkylpyrroles[10].

The retention behaviour of tri-B-alkylborazoles on Carbowax 4000 is of most interest in this respect, for with three N–H groups "sterically hindered" by a range of adjacent alkyl groups, they form a very convenient system for such a study. A useful method of comparing the behaviour of compounds in two different liquid phases is to plot the log t_R values against each other. For when this is done, the vertical distance between a compound and the paraffin line on the graph gives a measure of its specific retardation in the polar phase. Fig. 1 shows a plot for sixteen tri-B-alkylbora-
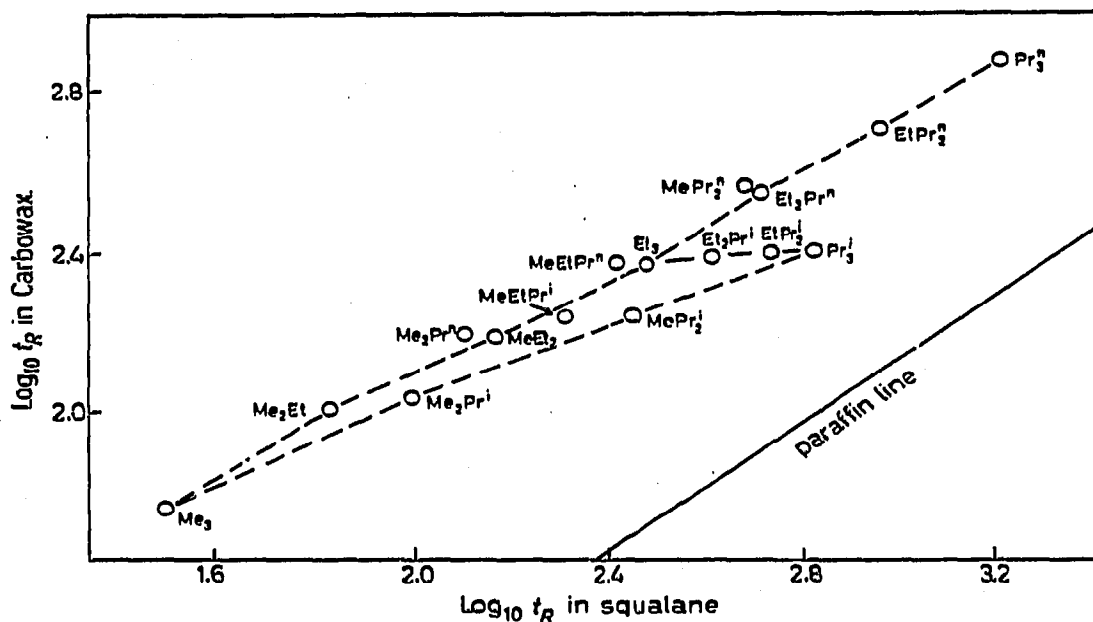

Fig. 1. Comparison of tri-B-alkylborazole retention times on Carbowax 4000 and on squalane.

zoles. The distances of the symmetrical tri-B-alkylborazoles from the paraffin line were divided by 3, to give four distances representing (if the theory is correct) the

effect of each alkyl group on the retardations due to the free N–H groups. In log t_R units these are:

Me 0.29; Et 0.22; Pr^n 0.19; Pr^i 0.14.

As expected the "steric effects" are in the order $Pr^i > Pr^n > Et > Me$. When the distance of mixed tri-B-alkylborazoles from the paraffin line are compared with those calculated by simply adding the individual alkyl group values, very good agreement is obtained (Table IX). Thus, if the log t_R values of tri-B-alkylborazoles are known in squalane, their retention times in Carbowax 4000 can be quite accurately predicted.

TABLE IX

RETARDATIONS OF TRI-B-ALKYLBORAZOLES ON CARBOWAX 4000

Tri-B-alkylborazole	Distance (log t_R units)		Tri-B-alkylborazole	Distance (log t_R units)	
	(obs.)	(calc.)		(obs.)	(calc.)
$EtPr^iPr^i$	0.49	0.50	$MePr^nPr^n$	0.68	0.67
$MePr^iPr^i$	0.56	0.57	$MeEtPr^n$	0.71	0.70
$EtEtPr^i$	0.57	0.58	$MeMePr^i$	0.71	0.72
$EtPr^nPr^n$	0.61	0.60	MeEtEt	0.74	0.73
$EtEtPr^n$	0.65	0.63	$MeMePr^n$	0.78	0.77
$MeEtPr^i$	0.66	0.65	MeMeEt	0.80	0.80

CONCLUSION

The simple correlations presented in this paper suggest that it should be possible to predict with reasonable accuracy the retention data of a very large number of other compounds. These will probably include (1) further alkyl-substituted silanes, germanes, digermanes and borazoles, (2) similar alkyl derivatives of methane, benzene, stannane, plumbane, and possibly other simple hydrides, and (3) alkyl derivatives of catenated hydrides. In connection with (2) it may be noted that many silane, germane and borazole derivatives can be more readily synthesised than their organic analogues. In connection with (3) we can report that we have some evidence for the existence of several alkyltrigermanes and for decamethyltetragermane with retention data as predicted.

Apart from the borazole–Carbowax interactions the retention patterns have been presented on an empirical basis. They must clearly, however, reflect subtle changes in intermolecular forces, for which there must be some basic structural explanation. So also the retention patterns provide us with a delicate method for examining subtle structural features in both inorganic and organic chemistry.

SUMMARY

Gas chromatographic retention data for a very large number of alkyl-substituted silanes, germanes, digermanes and borazoles are presented in terms of a few retention parameters and compared with the retention and boiling point data for hydrocarbon analogues.

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