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GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

VI. DETERMINATION, CALCULATION AND CORRELATION OF KOVÁTS RETENTION INDICES FOR ALKYLALKOXYSILANES

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SUMMARY

Several equations for the calculation of the retention indices of alkylalkoxysilanes are given and discussed. It is shown that accurate values of retention indices can be calculated on the basis of group retention indices of alkyl and alkoxy groups bonded to silicon. Temperature dependences of retention indices and ΔI values are given, and a method for their estimation is described.

A linear relationship exists between the retention indices of homologous series of alkylalkoxysilanes and those of the corresponding tetraalkoxysilanes. When retention indices of alkylalkoxysilanes on Apiezon M are plotted against the corresponding values on XE-60, two main linear relationships are found, one referring to so-called homologous lines and the other to so-called structure lines.

INTRODUCTION

In five previous papers in this series, methods for the calculation of Kováts retention indices of tetraalkoxysilanes[1–3] and tetraalkylsilanes[4] were developed, and various interrelations between the retention indices and certain other physical constants were established[5]. The present paper deals with another kind of organosilicon compounds, *viz.* alkylalkoxysilanes, $R_nSi(OR)_{4-n}$, where R is a normal alkyl group and $n = 1$–3.

Retentions of alkylalkoxysilanes were previously reported by Thrash[6], but no attempt at a theoretical treatment of the data was made. Wurst and Churácek[7] measured a quantity called the silicon index (I_{Si}) for several alkylalkoxysilanes; however, it is not possible to derive retention indices from the reported silicon indices. Retention indices of some alkylalkoxysilanes were also given in papers by Garzó *et al.*[8] and Harvey and Patton[9]. Retention indices of some trimethylalkoxysilanes were recently reported by Rybkina *et al.*[10] and a linear relationship between these and the carbon number was demonstrated. It thus appears that available gas chromatograph-

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ic data for alkylalkoxysilanes are very scarce and quite insufficient to serve as a basis for the derivation of equations for retention index calculations. Accordingly, we prepared some sixty alkylalkoxysilanes, most of them methylalkoxysilanes and ethylalkoxysilanes, and measured their retention indices on two stationary phases.

EXPERIMENTAL

Apparatus and columns

The work was performed using a Varian Model 1400 gas chromatograph with a flame ionization detector. As the temperature scale on this instrument could not be read to better than ± 1°C, an auxiliary thermocouple and temperature gauge were used, which enabled the temperature to be measured to ± 0.1°C (Mettler TM 15).

Steel columns (2–4 m × 1/8 in. O.D.) were packed with either Apiezon M (Apiezon, U.K.) or cyanosilicon GE XE-60 (Applied Science Labs., State College, PA, U.S.A.), 4 and 5% (w/w), respectively, on acid-washed and DMCS-treated Chromosorb G, 80–100 mesh. The column length was chosen to give a maximum retention time of *ca.* 1 h. For further experimental details, see part I of this series.

Determination of retention indices

Retention indices were measured by means of a slope detector, constructed at this laboratory, which permitted the measurement of retention times to ± 0.1 sec. The method used for determining retention indices involved the use of a computer for simulating the bracketing of each compound in the sample by two *n*-alkanes (see also ref. 11).

Materials

All compounds investigated were prepared in this laboratory. The alkylalkoxysilanes were prepared either from alkylchlorosilanes or alkylalkoxysilanes, and alcohols, according to the reactions

$$R_xSiCl_{4-x} + (4-x)R'OH \rightarrow R_xSi(OR')_{4-x} + (4-x)HCl \quad (1)$$

$$R_xSi(OR')_{4-x} + y\,R''OH \xrightarrow{Na} R_xSi(OR'')_y(OR')_{4-x-y} + yR'OH \quad (2)$$

The first method is best suited to the preparation of simple alkylalkoxysilanes, *i.e.* compounds just containing one kind of alkoxy group. In the second method, the outcome of the reaction is governed by the ratio of the alcohol R'OH to the alkylalkoxysilane. Thus, it is possible to prepare either mixed alkylalkoxysilanes as shown in eqn. 2 or the simple ones, $R_xSi(OR'')_{4-x}$, by using the alcohol R''OH in excess and distilling the formed alcohol (R'OH) from the reaction mixture.

RESULTS AND DISCUSSION

Equation for the calculation of retention indices of mixed alkylalkoxysilanes

In a previous paper[1] it was shown that retention indices of mixed tetraalkoxysilanes could be calculated with fair accuracy from the following equation:

$$I(\mathrm{RO})_4\mathrm{Si} = \Sigma I(\mathrm{RO})\mathrm{Si} + \Sigma(n \cdot d \cdot k)_{\mathrm{RO-RO}} \quad (3)$$

According to eqn. 3 the retention index of a tetra-alkoxysilane can be obtained by adding up the group retention indices [I(RO)Si] of the four alkoxy groups bonded to the silicon atom. In order to adjust for the non-additivity of the group indices, correction terms $\Sigma(n \cdot d \cdot k)_{\mathrm{RO-RO}}$ have to be added. These correction terms take into account the mutual influence of unlike alkoxy groups on their group indices. A similar equation was later[4] shown to be valid for mixed tetraalkylsilanes, although the agreement between the calculated and the experimental values was worse than for mixed tetraalkoxysilanes.

If the same method of calculation is applied to mixed alkylalkoxysilanes* the following equation is obtained.

$$I[\mathrm{R}_x\mathrm{Si}(\mathrm{OR}')_y(\mathrm{OR}'')_{4-x-y}] = [y/(4-x)]\, I[\mathrm{R}_x\mathrm{Si}(\mathrm{OR}')_{4-x}] +$$

$$+ [(4-x-y)/(4-x)]\, I[\mathrm{R}_x\mathrm{Si}(\mathrm{OR}'')_{4-x}] + (n \cdot d \cdot k)_{\mathrm{R'O-R''O}} \quad (4)$$

where R,R'O and R"O are normal alkyl and alkoxy groups; x and y = 1 or 2; n = so-called combination number; d = difference in carbon number between combined alkoxy groups; k = constant dependent on the smallest alkoxy group in a combination.

The combination number is obtained by multiplying the numbers of the various alkoxy groups bonded to the silicon atom, *i.e.* $n = y(4-x-y)$. The k values (Table I) are taken from ref. 1, which means that the same k values are used for mixed alkylalkoxysilanes as for mixed tetraalkoxysilanes. The values of the retention indices for simple alkylalkoxysilanes used in eqn. 4, $I[\mathrm{R}_x\mathrm{Si}(\mathrm{OR}')_{4-x}]$ and $I[\mathrm{R}_x\mathrm{Si}(\mathrm{OR}'')_{4-x}]$, are the experimental values given in Tables II and III.

TABLE I

VALUES OF CONSTANT k IN EQN. 4

Smallest group present	*In combination with*	*Values of constant k*	
		Calc. of I_{160}^{ApM}	*Calc. of* $I_{160}^{Kováts}$
Me	RO	5.4	7.0
Et	RO	1.7	–
MeO	RO	3.1*	3.3*
EtO	RO	1.5*	1.5*
PrO	RO	0.8*	0.8*
BuO	RO	0.4*	0.4*
MeO	R	2.8	–
EtO	R	1.2	–

* These values of k were taken from Table V in ref. 1.

* The term "mixed" just applies to the alkoxy groups as only one kind of alkyl group is present in each alkylalkoxysilane *cf.* Tables II and III.

TABLE II

EXPERIMENTAL AND CALCULATED RETENTION INDICES OF ALKYLAKOXYSILANES ON APIEZON M AT 160°C

Compound	*Exptl.*	*Eqn. 5*		*Eqn. 4*		*Eqn. 13*	
		Calcd.	*Diff.*	*Calcd.*	*Diff.*	*Calcd.*	*Diff.*
$MeSi(OMe)_3$	624	599	−25			624	0
$MeSi(OEt)_3$	772	759	−13			774	+2
$MeSi(OPr)_3$	1015	1010	− 5			1018	+3
$MeSi(OBu)_3$	1271	1270	− 1			1272	+1
$MeSi(OPe)_3$	1538	1542	+ 4			1539	+1
$MeSi(OHex)_3$	1808	1820	+12			1811	+3
$MeSi(OHept)_3$	2085	2205	+20			2083	−2
$MeSi(OMe)(OBu)_2$	1078	1065	−13	1074	−4	1075	−3
$MeSi(OMe)_2OHept$	1146	1135	−11	1148	+2	1148	+2
$MeSi(OEt)_2OPe$	1035	1034	− 1	1036	+1	1037	+2
$MeSi(OEt)(OPe)_2$	1290	1290	0	1292	+2	1292	+2
$MeSi(OPr)_2OHex$	1283	1285	+ 2	1284	+1	1287	+4
$EtSi(OMe)_3$	723	733	+10			726	+3
$EtSi(OEt)_3$	859	868	+ 9			862	+3
$EtSi(OPr)_3$	1100	1108	+ 8			1104	+4
$EtSi(OBu)_3$	1353	1357	+ 4			1355	+2
$EtSi(OPe)_3$	1614	1618	+ 4			1618	+4
$EtSi(OHex)_3$	1882	1885	+ 3			1886	+4
$EtSi(OEt)_2OPr$	939	951	+12	942	+3	945	+6
$EtSi(OEt)_2OBu$	1028	1040	+12	1032	+4	1032	+4
$EtSi(OEt)(OPr)_2$	1021	1031	+10	1023	+2	1026	+5
$EtSi(OEt)(OBu)_2$	1191	1199	+ 8	1194	+3	1196	+5
$PrSI(OMe)_3$	805	808	+ 3			806	+1
$PrSi(OEt)_3$	933	939	+ 6			936	+3
$BuSi(OMe)_3$	895	890	− 5			891	−4
$BuSi(OEt)_3$	1013	1017	+ 4			1016	+3
$PeSi(OMe)_3$	985	982	− 3			989	+4
$PeSi(OEt)_3$	1102	1103	+ 1			1106	+4
$Me_2Si(OMe)_2$	576	539	−37			573	−3
$Me_2Si(OEt)_2$	678	657	−21			677	−1
$Me_2Si(OPr)_2$	847	835	−12			846	−1
$Me_2Si(OBu)_2$	1024	1019	− 5			1022	−2
$Me_2Si(OPe)_2$	1209	1211	+ 2			1207	−2
$Me_2Si(OHex)_2$	1396	1407	+11			1395	−1
$Me_2Si(OHept)_2$	1587	1603	+16			1584	−3
$Me_2Si(OMe)OHept$	1098	1089	− 9	1100	+2	1097	−1
$Me_2Si(OEt)OHex$	1042	1038	− 4	1043	+1	1042	0
$Me_2Si(OPr)OPe$	1027	1025	− 2	1029	+2	1028	+1
$Me_2Si(OPr)OHept$	1218	1222	+ 4	1219	+1	1218	0
$Me_2Si(OBu)OHex$	1210	1214	+ 4	1211	+1	1210	0
$Et_2Si(OMe)_2$	795	801	+ 6			793	−2
$Et_2Si(OEt)_2$	878	886	+ 8			879	+1
$Et_2Si(OPr)_2$	1047	1050	+ 3			1045	−2
$Et_2Si(OBu)_2$	1216	1219	+ 3			1215	−1
$Et_2Si(OPe)_2$	1394	1397	+ 3			1397	+3
$Et_2Si(OHex)_2$	1580	1577	− 3			1580	0
$Pe_2Si(OMe)_2$	1296	1284	−12			1293	−3

TABLE II (*continued*)

Compound	*Exptl.*	*Eqn. 5*		*Eqn. 4*		*Eqn. 13*	
		Calcd.	*Diff.*	*Calcd.*	*Diff.*	*Calcd.*	*Diff.*
$Pe_2SiO(OEt)_2$	1354	1349	− 5			1354	0
Me_3SiOMe	506	480	−26			505	−1
Me_3SiOEt	558	544	−14			559	+1
Me_3SiOPr	645	638	− 7			647	+2
Me_3SiOBu	741	736	− 5			738	−3
Me_3SiOPe	836	837	+ 1			834	−2
$Me_3SiOHex$	932	941	+ 9			932	0
$Me_3SiOHept$	1030	1044	+14			1029	−1
Et_3SiOMe	858	865	+ 7			858	0
$EtSiOEt$	901	904	+ 3			899	−2
Et_3SiOPr	986	988	+ 2			984	−2
Et_3SiOBu	1076	1074	− 2			1072	−4
Et_3SiOPe	1169	1165	− 4			1165	−4
$Et_3SiOHex$	1262	1257	− 5			1259	−3
$Et_3SiOHept$	1358	1349	− 9			1354	−4
Bu_3SiOEt	1337	1334	− 3			1333	−4

In order to demonstrate the application of eqn. 4, the retention index of $MeSi(OMe)_2OHept$ (Me = methyl; Hept = heptyl) will be calculated.

$$I^{ApM}MeSi(OMe)_2OHept = (\tfrac{2}{3})I^{ApM}MeSi(OMe)_3 + (\tfrac{1}{3})I^{ApM}MeSi(OHept)_3 + (n \cdot d \cdot k)_{MeO-HeptO}$$

The combination number, n, is equal to 2 (2 · 1) as there are two MeO groups and one HeptO group. The difference in carbon number, d, between Me and Hept is 6 and k = 3.1, because MeO is the smallest alkoxy group present (Table I). By inserting the retention indices of the methyltrialkoxysilanes, taken from Table II, and adding the correction term (2 · 6 · 3.1) = 37.2) the retention index of $MeSi(OMe)_2OHept$ is calculated to be 1148. The experimental value is 1146.

The retention indices of several mixed alkylalkoxysilanes, calculated according to eqn. 4, are given in Tables II and III. The agreement between the experimental and calculated values is good, the mean deviation being 1.9 index units for the fourteen Apiezon M index measurements and 2.0 index units for the nine XE-60 values.

Equations for the calculation of retention indices of simple and mixed alkylalkoxysilanes

Eqn. 4 can be applied only to the calculation of retention indices of mixed alkylalkoxysilanes. Furthermore, a prerequisite is that the retention indices of the corresponding simple alkylalkoxysilanes are known. However, it was our aim to try to derive equations that permitted the calculation of retention indices of mixed as well as simple alkylalkoxysilanes from the group retention indices of the alkyl and

TABLE III

EXPERIMENTAL AND CALCULATED RETENTION INDICES OF ALKYLALKOXYSILANES ON XE-60 AT 160°C

Compound	*Exptl.*	*Eqn. 5*		*Eqn. 4*		*Eqn. 13*	
		Calcd.	*Diff.*	*Calcd.*	*Diff.*	*Calcd.*	*Diff.*
$MeSi(OMe)_3$	837	802	−35			842	+5
$MeSi(OEt)_3$	921	898	−23			921	0
$MeSi(OPr)_3$	1148	1138	−10			1150	+2
$MeSi(OBu)_3$	1399	1395	− 4			1398	−1
$MeSi(OPe)_3$	1666	1672	+ 6			1668	+2
$MeSi(OHex)_3$	1937	1953	+16			1940	+3
$MeSi(OHept)_3$	2215	2238	+23			2214	−1
$MeSi(OMe)(OBu)_2$	1234	1217	−17	1231	−3	1232	−2
$MeSi(OMe)_2OHept$	1337	1321	−16	1336	−1	1340	+3
$MeSi(OEt)_2OPe$	1180	1165	−15	1178	−2	1179	−1
$MeSi(OEt)(OPe)_2$	1426	1423	− 3	1427	+1	1428	+2
$MeSi(OPr)_2OHex$	1416	1414	− 2	1416	0	1418	+2
$Me_2Si(OMe)_2$	732	681	−51			734	+2
$Me_2Si(OEt)_2$	789	759	−30			789	0
$Me_2Si(OPr)_2$	951	932	−19			949	−2
$Me_2Si(OBu)_2$	1126	1118	− 8			1122	−4
$Me_2Si(OPe)_2$	1310	1317	+ 7			1310	0
$Me_2Si(OHex)_2$	1499	1518	+19			1501	+2
$Me_2Si(OHept)_2$	1688	1722	+34			1690	+2
$Me_2Si(OMe)OHept$	1234	1221	−13	1230	−4	1232	−2
$Me_2Si(OPr)OPe$	1135	1138	+ 3	1132	−3	1131	−4
$Me_2Si(OPr)OHept$	1322	1329	+ 7	1323	+1	1321	−1
$Me_2Si(OBu)OHex$	1315	1319	+ 4	1312	−3	1312	−3
Me_3SiOPr	710	699	−11			712	+2
Me_3SiOBu	805	799	− 6			802	−3
Me_3SiOPe	900	905	+ 5			900	0
$Me_3SiOHex$	996	1013	+17			1000	+4
$Me_3SiOHept$	1095	1122	+27			1095	0

alkoxy groups bonded to the silicon atom. In a first attempt the same principle of calculation as in eqns. 3 and 4 was used:

$$I[R_xSi(OR')_{4-x}] = \Sigma I(RSi) + \Sigma I(R'OSi) + \Sigma(n \cdot d \cdot k)_{R'O-R'O} + \\ + \Sigma(n \cdot d \cdot k)_{R-R'O} \quad (5)$$

where R denotes a normal alkyl group; R'O denotes normal alkoxy groups; x = 1–3; n, d and k have the same meaning as before.

According to eqn. 5, the retention index of an alkylalkoxysilane can be obtained by adding up the group retention indices of the alkyl and alkoxy groups obtained from the retention indices of the corresponding symmetrical compounds, *i.e.* tetraalkyl- and tetraalkoxysilanes, by division by four. In order to correct for the non-additivity of the group indices, correction terms have to be added. These correction terms take into account not only the mutual influences of unlike alkoxy groups on their group indices, but also the reciprocal influences between alkyl and

alkoxy groups on their indices. Since only compounds with one and the same alkyl group (R) are considered, no correction term for unlike alkyl groups is included.

The group retention indices of the alkyl and alkoxy groups are taken from Table IV. The values of k are given in Table I. When eqn. 5 was applied to the calculation of the retention indices of the alkylalkoxysilanes in Tables II and III, the mean deviation between experimental and calculated indices was found to be 8 index units for the 63 Apiezon M values and 15 index units for the 28 XE-60 values. It is evident that eqn. 5 does not allow the calculation of accurate retention indices for alkylalkoxysilanes from group retention indices.

TABLE IV

GROUP RETENTION INDICES* AND GROUP ΔI VALUES OF n-ALKOXY GROUPS AND n-ALKYL GROUPS IN SYMMETRICAL TETRAALKOXYSILANES AND TETRAALKYLSILANES, RESPECTIVELY

R	I^{ApM}_{160} (RSi)	I^{XE}_{160} (RSi)	ΔI_{160} (RSi)	I^{ApM}_{160} $(RO)Si$	I^{XE}_{160} $(RO)Si$	ΔI_{160} $(RO)Si$
Me	105	109.4	4.3	164.5	231.0	66.5
Et	230.6	237.0	6.4	212.5	256.0	43.5
Pr	298.2	301.1	2.9	290.8	328.8	38.0
Bu	371.4	377.2	5.8	372.0	407.5	35.5
Pe	455.0	461.8	6.8	457.5	493.0	35.5
Hex				544.5	579.5	35.0
Hept				631.8	667.5	35.7

* Obtained from the retention indices of symmetrical tetraalkyl[4] and tetraalkoxysilanes[1] by division by four and used in eqns. 4, 5 and 13.

In a previous paper[2], dealing with open tubular column retention indices of tetraalkoxysilanes, it was shown that very accurate indices could be calculated by using a modification of eqn. 3. In the modified version of this equation, the correction term was based on differences in retention index instead of on differences in carbon number. In the following it will be shown that a similar method can be used for the accurate calculation of the retention indices of alkylalkoxysilanes.

A linear relationship according to eqn. 6 holds for the retention indices of simple alkylalkoxysilanes and corresponding symmetrical tetraalkoxysilanes:

$$I[R_xSi(OR')_{4-x}] = p_xI(R'O)_4Si + q_x \quad (6)$$

where $R' \geq R$; $x = 1, 2$ or 3; R_x = the fixed part of the alkylalkoxysilane; $(R'O)_{4-x}$ = the changing part of the alkylalkoxysilane, *i.e.* R'O = MeO, EtO, *n*-PrO etc.; p_x and q_x are constants.

Table V gives the values of p_x and q_x in eqn. 6 and the correlation coefficients r of six homologous series of compounds measured on the Apiezon M column and of three homologous series measured on the XE-60 column. It can be seen that a very good linear relationship exists, especially for the Apiezon M retention indices.

In order to calculate the retention indices of alkylalkoxysilanes belonging to the three series $R_xSi(OR')_{4-x}$ (x = 1–3) from the retention indices of tetraalkoxysilanes, $Si(OR')_4$, three p_x constants and three q_x constants are needed for each sta-

TABLE V

VALUES OF p_x AND q_x IN EQN. 6 AND OF THE CORRESPONDING CORRELATION COEFFICIENT r

R	x	*Apiezon M, 160°C*			*XE-60, 160°C*		
		p_x	q_x	r	p_x	q_x	r
Me	3	0.2812	320.3	0.99995	0.2818	343.5	0.99975
	2	0.5411	218.7	1.00000	0.5474	229.5	0.99997
	1	0.7809	109.1	0.99999	0.7897	108.0	0.99997
Et	3	0.2723	669.8	0.99999			
	2	0.5269	431.7	0.99998			
	1	0.7704	204.7	1.00000			

tionary phase. However, it can be shown that the p_x values for the three series are related and that the same is true for the q_x values. This fact reduces the number of constants necessary for calculating the linear relationship in eqn. 6.

If the group retention indices were additive, the following relationship should hold:

$$I[R_xSi(OR')_{4-x}] = [(4-x)/4]\, I(R'O)_4Si + [x/4]I(R_4Si) \quad (7)$$

As $x = 1$, 2 or 3, $(4-x)/4$ will become 0.75, 0.50 or 0.25, and $x/4$ will become 0.25, 0.50 or 0.75. The former values correspond to p_x in eqn. 6. Comparison with, for example, the Apiezon M values of $Me_xSi(OR')_{4-x}$ in Table II confirms that the group retention indices are non-additive. We can write

$(x = 1)\ p_x = 0.7809 = 0.75 + 0.0309 = 0.75 + 3 \cdot 0.0103$
$(x = 2)\ p_x = 0.5411 = 0.50 + 0.0411 = 0.50 + 4 \cdot 0.0103$
$(x = 3)\ p_x = 0.2812 = 0.25 + 0.0312 = 0.25 + 3 \cdot 0.0104$

Accordingly, the general equation for calculating p_x can be written

$$p_x = p_t + n \cdot k' \quad (8)$$

where p_t = the theoretical p value, $(4-x)/4$ (x = 1–3); n = the combination number = $x(4-x)$, *i.e.* 3 or 4; k' = constant dependent on the kind of R group, *i.e.* Me or Et.

q_x can be treated in a similar manner. Thus we can write

$$q_x = q'_x I(R_4Si) \quad (9)$$

and the general equation for calculating q'_x will become

$$q'_x = q'_t - n \cdot k'' \quad (10)$$

where q'_t = the theoretical q' value $x/4$ (x = 1–3) and n and k'' have the same meaning as n and k' in eqn. 8.

By combining eqns. 6, 8, 9 and 10 we obtain eqn. 11 for calculating the retention indices of simple alkylalkoxysilanes with alkyl groups R and alkoxy groups R'O.

$$I[R_xSi(OR')_{4-x}] = [x/4]\, I(R_4Si) + [(4-x)/4]\, I(R'O)_4Si + \\ + n[k'_{R-R'O} I(R'O)_4Si - k''_{R-R'O} I(R_4Si)] \quad (11)$$

This equation can also be written

$$I[R_xSi(OR')_{4-x}] = xI(RSi) + (4-x)I(R'O)Si + \\ + 4x(4-x)[k'_{R-R'O} I(R'O)Si - k''_{R-R'O} I(RSi)] \quad (12)$$

The values of k' and k'', calculated from p_x and q_x, are dependent on the smallest group in the combination R–R'O. Some p_x and q_x, values are given in Table V. The group retention indices I(RSi) and I(R'O)Si are taken from Table IV.

Eqn. 12 holds only for simple alkylalkoxysilanes. In order for it to be valid for mixed alkylalkoxysilanes, the mutual influences of unlike alkoxy groups on their group indices must be considered:

$$I[R_xSi(OR')_y(OR'')_{4-x-y}] = xI(RSi) + yI(R'O)Si + \\ + (4-x-y)I(R''O)Si + 4xy[k'_{R-R'O} I(R'O)Si - k''_{R-R'O} I(RSi)] + \\ + 4x(4-x-y)[k'_{R-R''O} I\,(R''O)Si - k''_{R-R''O} I(RSi)] + \\ + 4y(4-x-y)[k'_{R'O-R''O} I(R''O)Si - k''_{R'O-R''O} I(R'OSi)] \quad (13)$$

Comparison with eqn. 5 shows that $d \cdot k$ has been exchanged for $4[k'_{R-R'O} I(R'O)Si - k''_{R-R'O} I(RSi)]$ and the corresponding correction terms for the interactions between the R–R''O and R'O–R''O groups. In order to simplify the calculation we constructed a table of correction coefficients b:

$$b = 4[k' I(YSi) - k'' I(XSi)] \quad (14)$$

where X denotes the smallest group in a combination (Me or Et or MeO to BuO), and Y is a larger group. Values of k' and k'' to be used in this calculation are collected in Table VI and some b values are given in Table VII.

In order to illustrate the application of eqn. 13, the retention index of $MeSi(OMe)_2OHept$ will be calculated.

$$I^{ApM}[MeSi(OMe)_2OHept] = I^{ApM}(MeSi) + I^{ApM}(HeptOSi) + \\ 2I^{ApM}(MeO)Si + 2b_{Me-MeO} + b_{Me-HeptO} + 2b_{MeO-HeptO}$$

Insertion of the group retention indices from Table IV and the b values from Table VII gives the retention index of $MeSi(OMe)_2OHept$ as 1148. The experimental value is 1146. The retention indices calculated according to eqn. 13 are listed in Tables II

TABLE VI

VALUES OF k' AND k'' TO BE USED IN THE CALCULATION OF THE CORRELATION COEFFICIENT $b = 4[k'I(YSi) - k''I(XSi)]$ WHERE $I(XSi) < I(YSi)$.

X	*Y*	*Apiezon M, 160°C*		*XE-60, 160°C*	
		k'	*k''*	*k'*	*k''*
Me	RO	0.0103	−0.0042	0.0125	−0.0040
Et	RO	0.0070	0.0084		
MeO	RO	0.0094	0.0071	0.0099	0.0070
EtO	RO	0.0049	0.0056	0.0050	0.0052
PrO	RO	0.0028	0.0031	0.0032	0.0036
BuO	RO	0.0015	0.0015	0.0015	0.0016
MeO	R	0.0144	0.0191		
EtO	R	0.0075	0.0105		

and III. The agreement between experimental and calculated values is satisfactory, the mean deviation being 2.3 index units for the 63 alkylalkoxysilanes measured on the Apiezon M stationary phase and 1.9 index units for the 28 compounds measured on the XE-60 stationary phase.

It thus appears that eqn. 13 is considerably more reliable than eqn. 5 and permits fairly accurate calculation of the retention indices of alkylalkoxysilanes from the constituent group indices. This study does not concern alkylalkoxysilanes in which the alkyl groups as well as the alkoxy groups are mixed, *i.e.* R'R"Si(OR')OR". However, it is believed that by applying the same principles as above and extending eqn. 13 with a correction term for the mutual influences of the two alkyl groups on their group retention indices, an equation could be obtained that would hold for this kind of alkylalkoxysilane. At present there are no experimental retention indices available for testing such an equation.

ΔI values of alkylalkoxysilanes

Kováts[12] denoted the difference between a polar and a non-polar retention index of a compound its ΔI value, and has shown it to be characteristic of the struc-

TABLE VII

VALUES OF THE CORRECTION COEFFICIENT b IN VARIOUS COMBINATIONS (XSiY)

Column	*Smallest group (X)*	*In combination with (Y)*										
		Et	*Pr*	*Bu*	*Pe*	*OMe*	*OEt*	*OPr*	*OBu*	*OPe*	*OHex*	*OHept*
Apiezon M	Me					8.5	10.5	13.7	17.0	20.5	24.1	27.5
	Et						(−1.8)	0.4	2.7	5.1	7.5	10.0
	MeO	0.71	4.6	8.8	13.6		3.3	6.2	9.3	12.5	15.8	19.1
	EtO	−2.0	0.2	2.2	4.7			0.9	2.5	4.2	5.9	7.6
	PrO								0.6	1.5	2.5	3.5
	BuO									0.5	1.0	1.6
XE-60	Me					13.3	14.6	18.2	22.1	26.4	30.7	34.1
	MeO						3.7	6.6	9.7	13.1	16.5	20.0
	EtO							1.3	2.8	4.5	6.3	8.0

TABLE VIII

EXPERIMENTAL AND CALCULATED (EQN. 13) ΔI VALUES OF ALKYLALKOXYSILANES

$\Delta I = I_{160}^{XE\text{-}60} - I_{160}^{ApM}$.

Compound	*Exptl.*	*Calcd.*	*Diff.*
$MeSi(OMe)_3$	213	219	+6
$MeSi(OEt)_3$	149	147	−2
$MeSi(OPr)_3$	133	132	−1
$MeSi(OBu)_3$	128	126	−2
$MeSi(OPe)_3$	128	127	−1
$MeSi(OHex)_3$	129	127	−2
$MeSi(OHept)_3$	130	132	+2
$MeSi(OMe)(OBu)_2$	156	157	+1
$MeSi(OMe)_2OHept$	191	192	+1
$MeSi(OEt)_2OPe$	145	142	−3
$MeSi(OEt)(OPe)_2$	136	136	0
$MeSi(OPr)_2OHex$	133	131	−2
$Me_2Si(OMe)_2$	156	161	+5
$Me_2Si(OEt)_2$	111	112	+1
$Me_2Si(OPr)_2$	104	103	−1
$Me_2Si(OBu)_2$	102	100	−2
$Me_2Si)(OPe)_2$	101	103	+2
$Me_2Si(OHex)_2$	103	106	+3
$Me_2Si(OHept)_2$	101	106	+5
$Me_2Si(OMe)OHept$	136	135	−1
$Me_2Si(OPr)OPe$	108	103	−5
$Me_2Si(Pr)OHept$	104	103	−1
$Me_2Si(OBu)OHex$	105	102	−3
Me_3SiOPr	65	65	0
Me_3SiOBu	64	64	0
Me_3SiOPe	64	66	+2
$Me_3SiOHex$	64	68	+4
$Me_3SiOHept$	65	66	+1

ture. A formula for calculating ΔI values of alkylalkoxysilanes is obtained by subtracting eqn. 13, valid for Apiezon M, from the same equation, valid for XE-60. Table VIII lists the calculated ΔI values of 28 alkylalkoxysilanes.

In the same way as the polarity of a compound can be expressed by its individual ΔI value, the constant ΔI value that the members of a homologous series attain when the carbon chain has reached a certain length can be used as a measure of the polarity of the series. Table IX summarizes the characteristic ΔI values of some homologous series, denoted ΔI_{hom}. Comparison with the ΔI value (17) of Me_4Si and

TABLE IX

ΔI_{hom} VALUES OF SOME HOMOLOGOUS METHYLALKOXYSILANE SERIES

Homologous series	$\Delta I_{hom}^{XE\text{-}ApM}$
$MeSi(OR)_3$	130
$Me_2Si(OR)_2$	101
Me_3SiOR	64

ΔI_{hom} (142) of $Si(OR)_4$ shows that the methylalkoxysilanes, as expected, are intermediate in polarity between Me_4Si and $Si(OR)_4$. It is also evident that the ΔI values can be used for deciding the ratio of alkyl to alkoxy groups in a methylalkoxysilane (see Table VIII and Fig. 1).

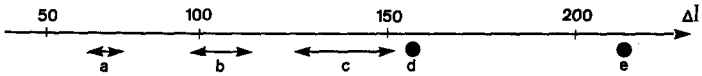

Fig. 1. $\Delta I_{160} = I^{XE}_{160} - I^{ApM}_{160}$ for homologous series of methylalkoxysilanes. (a) Me_3SiOR (R = Et-Hept); (b) $Me_2Si(OR)_2$ (R = Et-Hept); (c) $MeSi(OR)_3$ (R = Et-Hept); (d) $Me_2Si(OMe)_2$; (e) $MeSi(OMe)_3$.

Temperature dependence of retention indices

The measured change in retention index with temperature for some alkylalkoxysilanes is given in Table X. The retention index change is given as ten times the change of I per degree centigrade ($10dI/dT$). This method of reporting the variation in retention index presupposes an, at least approximately, linear change of I with T within the indicated temperature range. Thus, linear interpolation within the range

TABLE X

COMPARISON OF EXPERIMENTAL AND CALCULATED TEMPERATURE INCREMENTS OF SOME METHYLALKOXYSILANES

Compound	$10\frac{dI}{dT}$					
	Apiezon M			*XE-60*		
	Temp. range (°C)	*Exptl.*	*Calcd.*	*Temp. range (°C)*	*Exptl.*	*Calcd.*
$MeSi(OMe)_3$	100–160	−2.0	−2.1	60–120	−1.7	−0.4
$MeSi(OEt)_3$	100–160	−3.5	−3.4	60–160	−3.6	−3.5
$MeSi(OPr)_3$	100–120	−3.5	−3.4	100–160	−4.2	−4.1
$MeSi(OBu)_3$	120–220	−3.9	−4.5	140–180	−6.3	−5.3
$MeSi(OPe)_3$	160–220	−3.3	−4.5	140–200	−5.2	−5.3
$MeSi(OHex)_3$	160–220	−3.3	−4.8	160–200	−5.0	−6.0
$MeSi(OHept)_3$	160–220	−4.0	−5.4	160–200	−5.5	−6.5
$Me_2Si(OMe)_2$	100–160	−1.7	−1.4	60–120	−0.8	−0.3
$Me_2Si(OEt)_2$	100–160	−2.5	−2.8	60–120	−3.2	−2.4
$Me_2Si(OPr)_2$	100–160	−2.5	−2.8	60–120	−2.8	−2.8
$Me_2Si(OBu)_2$	100–200	−2.5	−3.0	100–160	−3.2	−3.5
$Me_2Si(OPe)_2$	160–220	−2.2	−3.0	120–160	−4.0	−3.5
$Me_2Si(OHex)_2$	160–220	−2.2	−3.3	140–220	−4.0	−4.0
$Me_2Si(OHept)_2$	160–220	−2.3	−3.6	140–200	−3.5	−4.4
Me_3SiOMe	100–160	−2.0	−0.7			
Me_3SiOEt	100–160	−2.0	−1.1			
Me_3SiOPr	100–160	−2.0	−1.1	60–100	−2.5	−1.4
Me_3SiOBu	100–160	−1.5	−1.5	80–120	−2.5	−1.8
Me_3SiOPe	100–160	−1.7	−1.5	80–120	−2.5	−1.8
$Me_3SiOHex$	100–180	−1.8	−1.6	80–120	−2.5	−2.0
$Me_3SiOHept$	100–180	−1.8	−1.8	100–140	−2.3	−2.2

to obtain retention indices at temperatures other than 160°C is possible, and some extrapolation outside the range is also permitted.

It can be seen that the change in index with temperature is negative and increases when the alkoxy group increases in size. This was previously also found to be the case for tetraalkoxysilanes, whereas the index change for tetra-alkylsilanes was negative or positive, depending on the structure, and considerably less than for tetraalkoxysilanes.

Approximate values of $10\mathrm{d}I/\mathrm{d}T$ of alkylalkoxysilanes can be calculated by adding values derived from $10\mathrm{d}I/\mathrm{d}T$ of tetraalkylsilanes[4] and tetraalkoxysilanes[2], respectively, by division by four.

However, the agreement between experimental and calculated values is not always good, mainly because the indices used for calculation, *viz.* those of Me_4Si and $(RO)_4Si$, were not measured in the same temperature range.

Retention indices of homologous series of mixed alkylalkoxysilanes versus retention indices of the simple counterparts

When the I_{160}^{ApM} values of homologous series of mixed alkylalkoxysilanes were plotted against the I_{160}^{ApM} values of the simple counterparts, the points were found to lie on straight lines, just as for the corresponding tetraalkoxysilanes. The slopes of the lines in the graph depend on whether one or two alkoxy groups are exchanged at a time and on the alkyl group. Similar plots are obtained for I_{160}^{XE}.

Two-phase plot

In the two-phase plot of I_{160}^{ApM} *versus* I_{160}^{XE}, two main linear relationships exist (see Fig. 2). The first refers to so-called homologous lines, which connect points in homologous series of alkylalkoxysilanes. Homologous lines for some methyl- and ethylalkoxysilane series are drawn in Fig. 2. The linear relationship in these series is a consequence of a linear relationship between the carbon number and I_{160}^{ApM} and I_{160}^{XE}, respectively.

The second linear relationship in Fig. 2 refers to so-called structure lines, which connect points with the same structure code. The structure code is written *a–b–d–e* where *a, b, d* and *e* are the number of CH_3, CH_2, CH and C groups present in the alkoxy groups. As this work concerns only normal alkoxy groups, *d* and *e* are always zero. Only experimental data were used to compile Fig. 2. However, it is possible to calculate the retention indices of some alkylalkoxysilanes belonging to the homologous and structure series in Fig. 2. The values obtained from eqn. 13 support the linear relationships derived in the figure. The available experimental material permits only a small number of structure lines to be drawn, *viz.* for mono- and dimethylalkoxysilanes.

In some previous communications from this laboratory the nature of homologous as well as structure lines of tetraalkoxy- and tetraalkylsilanes, respectively, were studied. Thus, it was established that for tetraalkoxysilanes, the homologous lines were well separated, whereas for tetraalkylsilanes they were united into one single line. On the other hand, tetraalkoxysilanes belonging to a structure group were found to lie on a single straight line whereas, for tetraalkylsilanes, there was a considerable scatter in the points representing a structure group. Since for the alkylalkoxysilanes studied in this work, the change between different compounds in the homologous

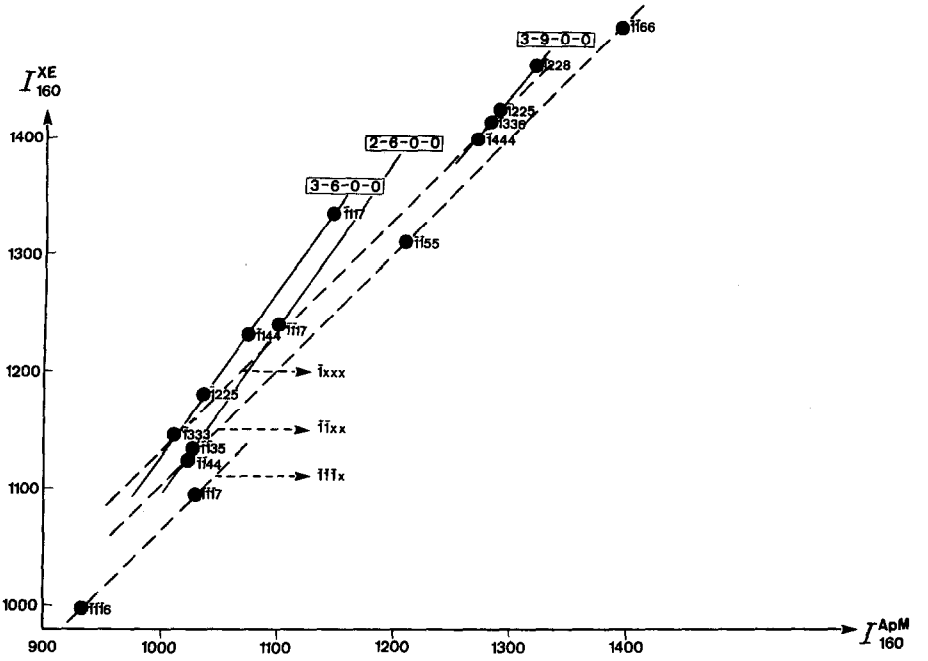

Fig. 2. Two-phase plot of I^{ApM}_{160} *versus* I^{XE}_{160}. Dashed lines are homologous lines; continuous lines are structure lines. $\bar{I}$ = Me; other digits = RO.

series and structure groups is brought about by a change in the alkoxy groups, it is not surprising to find that the points along homologous lines and structure lines, respectively, are arranged in a similar manner as for tetraalkoxysilanes.

CONCLUSIONS

The principles previously applied to the calculation of the retention indices of tetraalkyl- and tetraalkoxysilanes can also be applied to the calculation of the retention indices of alkylalkoxysilanes. Linear relationships exist between the retention indices of different homologous series of alkylalkoxysilanes or between retention indices of series of compounds on two different columns, as was previously established for tetraalkyl- and tetraalkoxysilanes.

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