Journal of Chromatography, 90 (1974) 35–40
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CHROM. 7200

GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOMETALLIC COMPOUNDS AND THEIR CARBON ANALOGUES

III. A STUDY OF KOVÁTS RETENTION INDICES FOR TETRAALKOXYSILANES CONTAINING BRANCHED ALKOXY GROUPS

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(Received November 6th, 1973)

SUMMARY

A method previously developed for the calculation of retention indices (Apiezon and XE-60 stationary phases) of mixed tetraalkoxysilanes with normal alkoxy groups was applied to some counterparts which also contained branched alkoxy groups (isopropoxy, isobutoxy and *sec.*-butoxy). It was found that the best agreement between experimental and calculated values was obtained for the Apiezon M retention indices, the average difference being about 3 index units. For the XE-60 retention indices, good agreement was obtained only for tetraalkoxysilanes that contain isobutoxy groups.

The linear relationship in the two-phase plot for retention indices of tetraalkoxysilanes, belonging to the same structure group (same number of CH_3, CH_2, CH and C groups), previously established for purely normal compounds, was found also to be valid for the structurally more complicated tetraalkoxysilanes studied in this work.

INTRODUCTION

The two previous papers[1,2] in this series were devoted to a study of Kováts retention indices of tetraalkoxysilanes with normal alkoxy groups. Methods for calculating retention indices were developed, and various interrelations between retention indices, as well as relationships between retention indices and certain physical constants, were established. In this paper, the previous studies are expanded to include tetraalkoxysilanes with branched alkoxy groups. It was of special interest to investigate whether the calculation methods valid for mixed tetraalkoxysilanes with normal alkoxy groups could also be applied to the counterparts with branched alkoxy groups. Another aim was to examine if the linear relationship in the two-phase plot, previously found to exist for normal tetraalkoxysilanes belonging to the same structure group[1], could be extended to include the present compounds.

EXPERIMENTAL

Packed columns (2–4 m × 1/8 in. O.D.) containing Apiezon M or cyanosilicone XE-60 as stationary phase were used in conjunction with a Varian Model 1400 gas chromatograph with a flame ionization detector. These columns were the same as those used in Part I, and further details can also be found in that paper[1]. The retention indices were determined using the computer method developed by the present author[3].

All compounds investigated were prepared in this laboratory. The symmetrical tetraalkoxysilanes were prepared from silicon tetrachloride and alcohols, and the mixed tetraalkoxysilanes by alkoxyl interchange between symmetrical tetraalkoxysilanes or by alcoholysis of the latter. Gaseous hydrogen chloride was used as a catalyst in both instances. The difficulty in separating certain compound mixtures by gas chromatography caused some limitations on the material available for the study.

RESULTS AND DISCUSSION

Retention indices and ΔI values of symmetrical tetraalkoxysilanes with branched alkoxy groups

Table I gives the retention indices and ΔI values of tetraisopropoxy-, tetraisobutoxy- and tetra-*sec.*-butoxysilanes. For comparison, the data for the corresponding normal tetraalkoxysilanes, taken from ref. 1, are also given. The retention indices of the branched compounds are considerably lower than those of the normal compounds, which was to be expected because of their lower boiling points. The marked difference between the ΔI values of normal and branched compounds reflects the increased shielding of the polar Si–O and C–O bonds in the latter, which increases their activity on the polar XE-60 stationary phase.

TABLE I

RETENTION INDICES AND ΔI VALUES FOR SYMMETRICAL BRANCHED AND NORMAL TETRAALKOXYSILANES

Compound	I_{160}^{ApM}	I_{160}^{XE}	$\Delta I_{160} = I_{160}^{\mathrm{XE}} - I_{160}^{\mathrm{ApM}}$
$(\text{iso-PrO})_4\text{Si}$	915	994	79
$(n\text{-PrO})_4\text{Si}$	1163	1315	152
$(\text{iso-BuO})_4\text{Si}$	1304	1410	106
$(sec.\text{-BuO})_4\text{Si}$	1264	1337	73
$(n\text{-BuO})_4\text{Si}$	1488	1630	142

Calculation of retention indices

An equation for calculating retention indices of mixed tetraalkoxysilanes on the basis of the symmetrical counterparts was given previously[1]:

$$I(\mathrm{RO})_4\mathrm{Si} = \Sigma I(\mathrm{RO})\mathrm{Si} + \Sigma(n \cdot d \cdot k)_{\mathrm{RO-RO}} \tag{1}$$

where

RO = n-alkoxy;
I(RO)Si = group retention index, obtained from the retention index of a symmetrical tetraalkoxysilane by division by four;
n = so-called combination number, obtained by multiplying the numbers of the various alkoxy groups in a combination. A combination is formed between any unlike alkoxy groups bonded to the silicon atom. Thus, in the tetraalkoxysilane $(RO)_nSi(OR')_{4-n}$, RO and R'O form a combination with the combination number $n(4-n)$. In the tetraalkoxysilane $(RO)_nSi(OR')_m(OR'')_{4-n-m}$, there are three combinations with the combination numbers $n \cdot m$, $n(4-n-m)$ and $m(4-n-m)$ (see also ref. 1);
d = carbon number difference between alkoxy groups in a combination;
k = constant, dependent on the smallest alkoxy group in a combination.

The second term in eqn. 1 can be considered as a correction term that accounts for the deviation of the sum of the group retention indices in the mixed tetraalkoxysilane from additivity. In the calculation of retention indices of the mixed tetraalkoxysilanes in Table II, it has been assumed that the constant k for a combination containing a branched alkoxy group is the same as when the alkoxy group is normal. Accordingly, isopropoxy is treated as an n-propoxy group and isobutoxy and *sec.*-butoxy as an n-butoxy group. The k values used were taken from Table V in ref. 1.

The best agreement between experimental and calculated values was obtained for the Apiezon M retention indices, the mean deviation being about 3 index units. Thus, it appears that the method used gives an at least approximately correct value for the correction term for the type of compound studied. For 5 of the 28 compounds, the deviation is 6 index units or more. All of these compounds contain *sec.*-butoxy groups. This deviation is considerably greater than the error in the retention index measurement, and it is concluded that eqn. 1 is less suited for the calculation of Apiezon M retention indices of mixed tetraalkoxysilanes with *sec.*-butoxy groups, than for those with isopropoxy or isobutoxy groups.

This fact is even more apparent for the XE-60 retention indices, where the difference between experimental and calculated values for *sec.*-butoxy silanes is considerable. Good agreement is obtained in this case only for mixed tetraalkoxysilanes with isobutoxy groups. As the calculated values for *sec.*-butoxy silanes are always too high, it is obvious that a better agreement should be attained by using smaller $k \cdot d$ values for the combinations methoxy–*sec.*-butoxy and ethoxy–*sec.*-butoxy, respectively.

To summarize, the results obtained warrant the conclusion that a successful application of eqn. 1 using the k values valid for n-alkoxy groups is dependent both on the type of branched alkoxy group and on the polarity of the stationary phase. On a polar stationary phase such as XE-60, better agreement between experimental and calculated values can be expected when the branching takes place at the β-carbon atom, than when the alkoxy group is branched at the α-carbon atom. On a non-polar phase such as Apiezon M, not only the position of branching but also the size of the

TABLE II

EXPERIMENTAL AND CALCULATED RETENTION INDICES FOR MIXED TETRAALKOXYSILANES CONTAINING BRANCHED ALKOXY GROUPS

Compound	I_{160}^{ApM}			I_{160}^{XE}			ΔI_{160}	*Structure code*
	Exptl.	*Calcd.*	*Diff.*	*Exptl.*	*Calcd.*	*Diff.*		
(MeO)$_3$SiOPr-iso	743	741	−2					5–0–1–0
(MeO)$_2$Si(OPr-iso)$_2$	813	812	−1					6–0–2–0
MeOSi(OPr-iso)$_3$	869	870	+1					7–0–3–0
(MeO)$_3$SiOBu-iso	851	848	−3	1077	1076	−1	226	5–1–1–0
(MeO)$_2$Si(OBu-iso)$_2$	1022	1018	−4	1206	1207	+1	184	6–2–2–0
MeOSi(OBu-iso)$_3$	1172	1171	−1	1314	1319	+5	142	7–3–3–0
(MeO)$_3$SiOBu-*sec.*	839	838	−1	1057	1057	0	218	5–1–1–0
(MeO)$_2$Si(OBu-*sec.*)$_2$	996	998	+2	1163	1171	+8	167	6–2–2–0
MeOSi(OBu-*sec.*)$_3$	1135	1141	+6	1252	1264	+12	117	7–3–3–0
(EtO)$_3$SiOBu-iso	974	973	−1	1131	1130	−1	157	5–4–1–0
(EtO)$_2$Si(OBu-iso)$_2$	1091	1089	−2	1231	1229	−2	140	6–4–2–0
EtOSi(OBu-iso)$_3$	1201	1200	−1	1324	1323	−1	123	7–4–3–0
(EtO)$_3$SiOBu-*sec.*	959	963	+4	1107	1111	+4	148	5–4–1–0
(EtO)$_2$Si(OBu-*sec.*)$_2$	1063	1069	+6	1182	1193	+11	119	6–4–2–0
EtOSi(OBu-*sec.*)$_3$	1164	1170	+6	1260	1268	+8	96	7–4–3–0
(PrO)$_3$SiOPr-iso	1103	1101	−2	1232	1235	+3	129	5–6–1–0
(PrO)$_2$Si(OPr-iso)$_2$	1040	1039	−1	1149	1155	+6	109	6–4–2–0
PrOSi(OPr-iso)$_3$	977	977	0	1066	1074	+8	89	7–2–3–0
(BuO)$_3$SiOBu-iso	1438	1442	+4	1573	1575	+2	135	5–10–1–0
(BuO)$_2$Si(OBu-iso)$_2$	1393	1396	+3	1517	1520	+3	124	6–8–2–0
BuOSi(OBu-iso)$_3$	1345	1350	+5	1460	1465	+5	115	7–6–3–0
(MeO)$_2$Si(OBu)OBu-iso	1066	1064	−2	1264	1262	−2	198	5–4–1–0
MeOSi(OBu)$_2$OBu-iso	1262	1263	+1	1428	1429	+1	166	5–7–1–0
MeOSi(OBu) (OBu-iso)$_2$	1216	1217	+1	1372	1374	+2	156	6–5–2–0
(MeO)$_2$Si(OBu)OBu-*sec.*	1054	1054	0	1242	1244	+2	188	5–4–1–0
MeOSi(OBu)$_2$OBu-*sec.*	1247	1253	+6	1402	1410	+8	155	5–7–1–0
MeOSi(OBu) (OBu-*sec.*)$_2$	1189	1197	+8	1324	1337	+13	135	6–5–2–0
(MeO)$_2$Si(OPr-iso)OPe	1056	1053	−3	1245	1245	0	189	5–4–1–0

group is of importance, as tetraalkoxysilanes that contain isopropoxy groups show better agreement than those that contain *sec.*-butoxy groups.

I_{160}^{ApM} *versus* I_{160}^{XE}

In the two-phase plot of I_{160}^{ApM} *versus* I_{160}^{XE} for normal tetraalkoxysilanes, two linear relationships were established[1]. One was between retention indices of members in homologous series and the other between retention indices of compounds that have the same structure code. The compounds available permit no linearity test for members in homologous series, but it is undoubtedly reasonable to assume that the relationship is linear to the same extent as for purely normal tetraalkoxysilanes.

In Table II, a structure code is given for each compound. This 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, respectively. As it was found in the previous work that normal tetraalkoxysilanes with the same structure code align themselves along straight lines, it was of interest to examine if the same rule was applicable to the structurally more complicated tetraalkoxysilanes studied in this work.

The retention indices of members of two structure groups with the codes 5–4–1–0 and 6–4–2–0 are plotted in Fig. 1, where the points are seen to lie on straight lines. This is also borne out by the correlation coefficients in Table III. The difficulties encountered in the gas chromatographic separation of various mixtures resulting from the synthesis of the tetraalkoxysilanes investigated have prevented the determination of retention indices for more than two compounds in each of the remaining four structure groups in Table III. However, the equations of the straight lines assumed to belong to these structure groups have nevertheless been calculated and are given in the table.

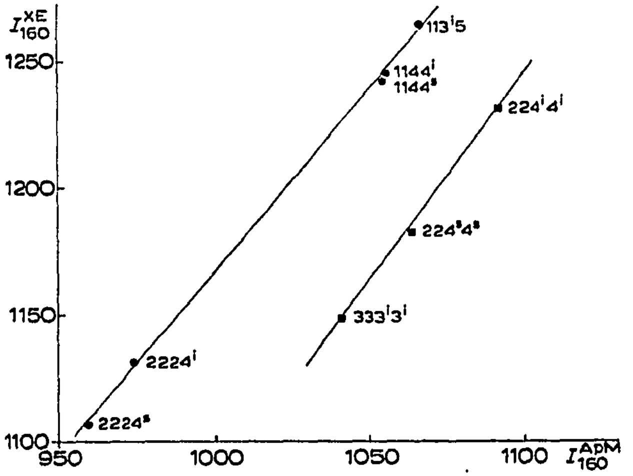

Fig. 1. Two-phase plot of I_{160}^{ApM} *versus* I_{160}^{XE}. Structure codes: ●, 5–4–1–0; ■, 6–4–2–0. The formula code denotes the alkoxy groups bonded to the silicon atom: 1 = methoxy, 2 = ethoxy, 3 = *n*-propoxy, 3^i = isopropoxy, 4^s = *sec*.-butoxy, etc.

TABLE III

CONSTANTS IN AND CORRELATION COEFFICIENTS OF THE LINEAR RELATIONSHIP $I_{160}^{XE} = k \cdot I_{160}^{ApM} + l$ FOR TETRAALKOXYSILANES WITH THE SAME STRUCTURE CODE *a–b–d*–0

Structure code	*Number of compounds*	*k*	*l*	*Correlation coefficient*
5–4–1–0	5	1.43	−264	0.9996
6–4–2–0	3	1.61	−530	0.9990
6–2–2–0	2	1.65	−484	
6–5–2–0	2	1.78	−790	
7–3–3–0	2	1.68	−650	
7–4–3–0	2	1.73	−753	

ACKNOWLEDGEMENT

The cooperation of Mrs. Kerstin Svensson in the experimental work is gratefully acknowledged.

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