

CHROM. 15,491

GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XXI*. CAPILLARY COLUMN STUDIES OF THE CHLORINATED PHENYL ACETATES

J. K. HAKEN*

Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

and

I. O. O. KORHONEN

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)

(Received November 4th, 1982)

SUMMARY

The gas chromatographic retention behaviour of the series of chlorinated phenyl acetates has been studied on SE-30 and OV-351 quartz capillary columns at 160, 180 and 200°C. Retention index measurements for each position of substitution together with the effect of increasing temperature on retention are discussed. The relative effect of polar and steric effects are considered and it is evident that major retention variations due to either effect do not occur.

INTRODUCTION

Gas chromatography of chlorinated esters has been the subject of extensive recent study. In particular, the separation of aliphatic esters¹⁻³ has been examined together with the effect of structure and of retention increments. Aromatic esters have not been extensively studied and several earlier reports are indicated in the work of Korhonen and Knuutinen⁴ concerning the gas chromatographic (GC) and GC-mass spectrometric (MS) studies of the acetate esters of chlorinated phenols where relative retention data obtained by temperature programming were used.

The interest in chlorinated phenyl derivatives has resulted from the environmental hazards associated with chlorophenols; these are of widespread origin and or necessity must be capable of estimation for regulatory purposes. Recent studies have employed glass capillary column GC, usually on a non-polar stationary phase, and in association with MS. Acetyl⁵⁻⁸, ethoxy^{9,10} and silyl ether^{7,11,12} derivatives have been used with electron-capture detection. The sensitivity to electron-capture detection has

* For Part XX, see ref. 3.

been increased by using a halogen-containing derivatization reagent, *i.e.* heptafluorobutyric anhydride¹³.

The work of Korhonen and Knuutinen⁴ considers for the first time the acetyl derivatives of all of the isomeric chlorinated phenols while the present work extends this earlier study and reports retention indices on both SE-30 and OV-351 capillary columns at 160, 180 and 200°C. The retention index increments for each position of substitution together with the effect of increasing temperature on the values are discussed.

EXPERIMENTAL

Analyses were performed on a Perkin-Elmer Sigma 3 instrument with the following operating conditions: injector and detector temperatures, 260 and 275°C, respectively; nitrogen flow-rate, 1 ml/min; split ratio, 1:25. The columns used were (1) vitreous silica (25 m × 0.22 mm I.D.) coated with SE-30 (SGE, North Melbourne, Australia) and (2) fused silica (25 m × 0.32 mm I.D.) coated with OV-351 (Orion Analytica, Espoo, Finland).

Retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector M2 microprocessor system, the dead volume being first determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs¹⁴.

Commercial chlorophenols (Fluka, Buchs, Switzerland) were converted into their acetyl derivatives by the method of Renberg and Lindström¹⁵. The products were identified by glass capillary GC-MS before GC analyses.

RESULTS AND DISCUSSION

Retention indices determined on both columns at 160, 180 and 200°C are shown in Tables I and II. Table III gives the total incremental effect due to the addition of a chlorine or chlorine atoms and an average effect due to each chlorine atom at each of the possible positions of attachment.

Examination of the SE-30 data shows that all the isomers with a particular number of chlorine atoms are eluted before the first isomer of the next series with one more substituent, and that with all compounds the retention increases with temperature and the elution order remains unaltered.

The structure of the isomers is shown below, the numbers or symbols used indicating the chlorinated positions relative to the carbonyl, with *ortho* as *o*, and *o'*, *meta* as *m* and *m'* and *para* as *p*.

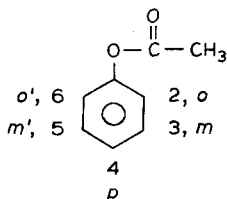


TABLE I
RETENTION INDICES OF CHLORINATED PHENYL ACETATES ON SE-30

Compound*	Temperature		
	160°C	180°C	200°C
PhAc	1008	1025	1033
2	1173	1192	1199
3	1198	1219	1228
4	1203	1224	1228
2,6	1296	1330	1396
2,4 + 2,5	1317	1351	1420
3,5	1334	1367	1441
2,3	1350	1384	1466
3,4	1377	1410	1494
2,4,6	1420	1454	1546
2,3,6	1463	1495	1591
2,3,5	1476	1506	1601
2,4,5	1481	1511	1606
2,3,4	1525	1552	1651
3,4,5	1543	1569	1667
2,3,5,6	1612	1633	1732
2,3,4,6	1617	1637	1735
2,3,4,5	1679	1694	1790
2,3,4,5,6	1808	1809	1899

* PhAc = phenyl acetate; the numbers indicate the chlorinated positions.

TABLE II
RETENTION INDICES OF CHLORINATED PHENYL ACETATES ON OV-351

Compound*	Temperature		
	160°C	180°C	200°C
PhAc	1633	1639	1664
2	1829	1838	1858
3	1848	1856	1876
4	1870	1878	1898
3,5	1964	1976	1993
2,6	1971	1985	2007
2,4 + 2,5	1986	1998	2016
2,4,6	2035	2050	2075
2,3	2052	2067	2093
3,4	2072	2086	2113
2,3,5	2117	2133	2160
2,4,5	2133	2150	2177
2,3,6	2139	2159	2187
3,4,5	2215	2236	2267
2,3,5,6	2225	2248	2281
2,3,4	2233	2254	2286
2,3,4,6	2236	2260	2294
2,3,4,5	2333	2358	2397
2,3,4,5,6	2401	2433	2479

* As shown in Table I.

TABLE III
INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION WITH TEMPERATURE

Compound*	Column		OV-351												f_{OV-351}								
	SE-30		180°C				200°C				160°C				180°C				200°C				f_{SE-30}
	$\Sigma \Delta I^{**}$	ΔI^{***}	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI	$\Sigma \Delta I$	ΔI			
2	165	165	167	167	166	166	166	166	196	196	199	199	199	199	194	194	199	199	194	194	1.56		
3	190	190	194	194	195	195	195	195	215	215	217	217	217	217	212	212	217	217	212	212	1.54		
4	195	195	199	199	199	199	199	199	237	237	329	329	329	329	234	234	329	329	234	234	1.55		
2,6	288	144	305	153	363	182	338	169	338	169	346	173	343	172	343	172	346	173	343	172	1.44		
2,4 + 2,5	309	155	326	163	387	194	353	178	353	178	359	180	352	176	352	176	359	180	352	176	1.51		
3,5	326	163	342	171	408	204	331	166	331	166	337	169	329	165	329	165	337	169	329	165	1.47		
2,3	342	171	359	180	433	216	419	210	419	210	428	214	429	215	429	215	428	214	429	215	1.52		
3,4	369	184	385	193	461	231	439	220	439	220	447	224	449	225	449	225	447	224	449	225	1.51		
2,4,6	412	137	429	143	513	171	402	134	402	134	411	137	411	137	411	137	411	137	411	137	1.43		
2,3,6	455	152	470	157	558	186	506	169	506	169	520	173	523	174	523	174	520	173	523	174	1.46		
2,3,5	468	156	481	160	568	189	484	161	484	161	494	165	496	165	496	165	494	165	496	165	1.43		
2,4,5	473	158	486	162	573	191	500	167	500	167	511	170	513	171	513	171	511	170	513	171	1.44		
2,3,4	517	172	527	176	618	206	600	200	600	200	615	205	622	207	622	207	615	205	622	207	1.46		
3,4,5	535	178	544	181	634	211	582	194	582	194	597	199	603	201	603	201	597	199	603	201	1.44		
2,3,5,6	604	151	608	152	699	175	592	148	592	148	609	152	617	154	617	154	609	152	617	154	1.38		
2,3,4,6	609	152	612	153	702	176	603	151	603	151	621	155	630	158	630	158	621	155	630	158	1.38		
2,3,4,5	671	168	669	167	757	189	700	175	700	175	719	180	733	183	733	183	719	180	733	183	1.39		
2,3,4,5,6	800	160	784	157	866	173	768	154	768	154	794	159	815	163	815	163	794	159	815	163	1.33		

* As shown in Table I.

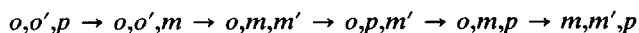
** Total retention index increase.

*** Retention index increase per chlorine atom.

The monochloro isomers (2, 3 and 4) are eluted according to their boiling points, the retention increasing with increase in the distance between the substituent and the carbonyl group (*i.e.* in the order: *o*-, *m*- and *p*-isomer). The difference in retention of the 3- and 4-isomer is small.

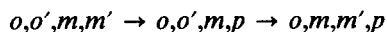
With the dichloro esters the lowest retention is shown by the 2,6-isomer where the substitution occurs in both positions *ortho* to the carbonyl group. Equivalent retention is shown by the 2,4- and 2,5-isomers with increased retention of the *meta*-disubstituted 3,5-isomer. Enhanced retention is observed by the 2,3-isomer due to some reinforcement of the polar effects by their close proximity, while the highest retention is shown by the 3,4-isomer. This is, as expected, from the monosubstituted esters and from the observation of enhanced retention of the 2,3-isomer. This effect of proximity is different from that observed with alkyl esters where the trend of increased retention with regard to the position of the carbonyl group is reduced by substitution of the adjacent carbon atoms.

The retention of the trichloro esters is shown below:



The behaviour completely follows that of the mono- and dichloro isomers.

Similar behaviour of the tetra-substituted esters occurs with the elution order being



Predictably the elution order of the isomers follows that of the earlier paper⁴, the elution of the 3,4- and 3,5-dichloroisomers being reversed, as previously reported on SE-30 glass capillary columns^{6,7}.

The retention on the more polar OV-351 stationary phase is predictably increased and with operation of polar forces on the phase as well as the solutes some overlap of species and some variation in elution order occurs. The incremental effects are shown in Table III while the elution sequences are shown in Fig. 1.

Elution of the monochloro esters remains unaltered although the retention of the *para*-isomer is increased more than with the other two isomers. With the dichloro esters the 2,6-isomer, *i.e.*, *o,o'*, is of greater retention than the 3,5-isomer (*m,m'*), the presence of the two chlorine groups adjacent to the carbonyl having a greater effect. Similarly, with the trichloro esters, the 2,3,6-isomer, *i.e.*, *o,o',m*, has a higher retention than the 2,3,5-isomer, *i.e.* *o,m,m'*, and the 2,3,4-isomer, *i.e.* *o,m,p*, is of greater retention than the 3,4,5-isomer, *i.e.* *m,m',p*. This follows the pattern of the simpler esters.

Considerable overlap exists with the tetrachloro esters, the trichloro esters with adjacent substituents having comparable retention with the tetrachloro esters with non-adjacent substituents, *i.e.* the 2,3,5,6- and 2,3,4,6-isomers, while the retention of the ester with adjacent halogen atoms *i.e.* the 2,3,4,5-isomer shows considerable enhancement.

The incremental effects of chlorine additions are shown in Table III. It is apparent that with both phases the incremental differences increase with temperature, also the incremental increases tend to be relatively constant with different levels of chlorine substitution and vary rather with the position of substitution. Molecules

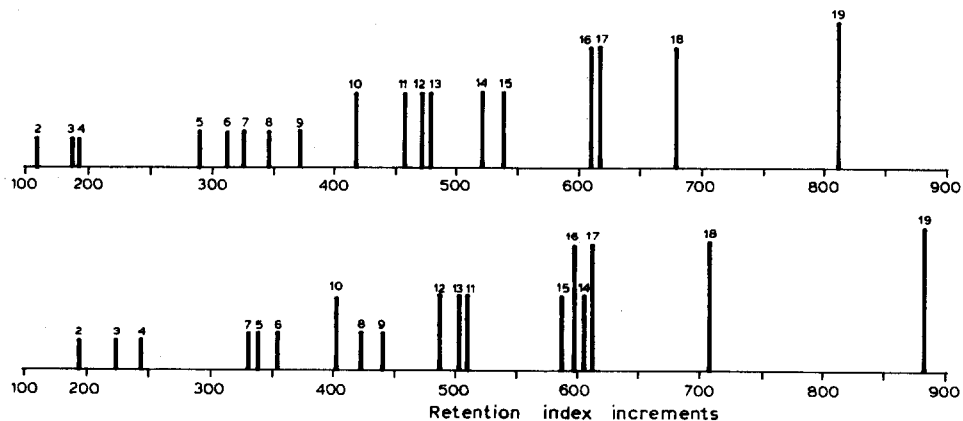


Fig. 1. Elution sequence and retention index increments of chlorinated phenol acetates on SE-30 (upper diagram) and OV-351 (lower diagram). The position of substitution is (2) 2, (3) 3, (4) 4, (5) 2,6, (6) 2,4 + 2,5, (7) 3,5, (8) 2,3, (9) 3,4, (10) 2,4,6, (11) 2,3,6, (12) 2,3,5, (13) 2,4,5, (14) 2,3,4, (15) 3,4,5, (16) 2,3,5,6, (17) 2,3,4,6, (18) 2,3,4,5, (19) 2,3,4,5,6.

with substitution in the *para*- and *meta*-positions, and particularly together, show the greatest retention.

With the low-polarity column it is evident that the incremental effect of a single chlorine atom is greatest, in agreement with several recent reports concerning the chlorinated aliphatic esters³. However with the aromatic esters the decrease is much less dramatic than with the aliphatic esters, where the substitution was on a single carbon atom rather than on adjacent sites.

Isomers with *ortho* or isolated substituents show the lowest incremental changes, the *ortho*-monochloro ester predictably showing the highest retention increment in the group, *i.e.* 160 index units. This is reduced to 144 units with *o,o'*-disubstitution and to 137 units with *o,o',p*-trisubstitution. The closest tetrasubstituted isomer, *i.e.* the 2,3,5,6-isomer, has a higher increment due to some enhancement by the adjacent substituents. This is evident from the trio *o,o' → o,m → m,p* with incremental increases of 144 → 171 → 184 retention index units.

With the polar phase the increments are generally increased with the effects indicated above being generally observed. Some minor variation in the elution order of several isomers is observed but this is largely due to further enhancement of retention on adjacent sites due to the more polar stationary phase.

The relative polar and steric effects have been previously discussed⁴. From the retention index ratios on the two columns shown in Table III it is evident that, while the previous conclusions are valid, major retention variations due to either polar or steric effects are not evident with the chlorinated isomers.

ACKNOWLEDGEMENT

I.O.O.K. wishes to express his gratitude to the Academy of Finland for financial support.

REFERENCES

- 1 I. O. O. Korhonen, *J. Chromatogr.*, 248 (1982) 69, and earlier parts of series.
- 2 I. O. O. Korhonen, *Chromatographia*, in press.
- 3 J. K. Haken, B. G. Madden and I. O. O. Korhonen, *J. Chromatogr.*, 256 (1983) 221.
- 4 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, in press.
- 5 R. H. Voss, J. T. Wearing, R. D. Mortimer, T. Kovacs and A. Wong, *Pap. Puu*, 12 (1980) 809.
- 6 R. C. C. Wegman and A. W. M. Hofstee, *Water Res.*, 13 (1979) 651.
- 7 W. Krijgsman and C. G. van de Kamp, *J. Chromatogr.*, 131 (1977) 412.
- 8 W. Ernst and K. Weber, *Chemosphere*, 11 (1978) 687.
- 9 K. Lindström and J. Nordin, *J. Chromatogr.*, 128 (1976) 13.
- 10 S.-Kachi, N. Yonese and Y. Yoneda, *Pulp Paper Can.*, 81 (1980) 105.
- 11 B. Holmbom, *Pap. Puu*, 9 (1980) 523.
- 12 B. Holmbom and K.-J. Lehtinen, *Pap. Puu*, 11 (1980) 673.
- 13 A. B. McKague, *J. Chromatogr.*, 208 (1981) 287.
- 14 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
- 15 L. Renberg and K. Lindström, *J. Chromatogr.*, 214 (1981) 327.