Journal of Chromatography, 265 (1983) 323–327
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,912

Note

Retention increments of isomeric chlorobenzenes

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(Received April 12th, 1983)

The chlorobenzene isomers are used extensively as intermediates in a wide range of chemical products. More recently their determination in environmental situations has become of considerable importance and chromatographic procedures have been widely reported for their determination in both trace and major amounts.

There are over 220 publications in which gas chromatography (GC) has been applied to the analysis of chlorobenzene. However, over 60% of these works refer to the separation of only one isomer. Relatively few publications[1–8] consider all the isomers, although the use of both capillary[3–5] and packed[6–8] columns with polar and non-polar stationary phases has been reported. Temperature programming and isothermal operation have been used, with retention times, relative retention times and retention ratios being variously reported.

The effect on retention of increasing chlorine substitution has not been reported and this paper shows the incremental effect in terms of retention indices on a non-polar (SE-30) and a polar (Carbowax 20M) capillary column. The elution order of the isomers is compared with that reported previously.

EXPERIMENTAL

Chlorobenzenes were commercial products (Fluka, Buchs, Switzerland).

GC analyses were carried out on a Varian Model 2400 gas chromatograph and on a Perkin-Elmer Sigma 3 instrument under the following operating conditions: glass capillary column (22 m × 0.30 mm I.D.) coated with 3% Carbowax 20M; a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 mm I.D.), supplied by SGE (North Melbourne, Australia); injector and detector temperatures, 275°C; splitting ratio, 1:20; and nitrogen carrier gas flow-rate, 1 ml/min. Retention data were recorded with a Hewlett-Packard Model 3390A reporting integrator.

The retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector MZ microprocessor system, the dead volume being first determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs[9].

0021-9673/83/$03.00

RESULTS AND DISCUSSION

The retention indices of the chlorobenzene isomers on SE-30 and Carbowax 20M, determined in each instance at 120, 140, 160 and 180°C, are shown in Tables I and II.

The elution order is as reported earlier using capillary columns coated with low-polarity stationary phases, *i.e.*, SP-2100[4] and SE-52[5], the isomers being eluted in order of to their boiling points. The closely related 1,2,3,5- and 1,2,4,5-tetrachloro isomers were not resolved any better in the earlier work in spite of the temperature programming used. Isothermal operation using packed columns with Lukopren G 1000[6], Apiezon L[7,8] and PPMS-4[7,8] again producing similar results.

TABLE I

RETENTION INDICES OF CHLOROBENZENE ISOMERS ON SE-30

Isomer	*Temperature (°C)*			
	120	*140*	*160*	*180*
	832	836	840	842
1,3-Di-	964	1013	1016	1021
1,4-Di-	970	1015	1016	1021
1,2-Di-	1005	1038	1050	1057
1,3,5-Tri-	1131	1144	1150	1159
1,2,4-Tri-	1177	1183	1193	1207
1,2,3-Tri-	1211	1217	1228	1247
1,2,3,5-Tetra-	1326	1329	1344	1367
1,2,4,5-Tetra-	1326	1329	1344	1367
1,2,3,4-Tetra-	1366	1371	1388	1412
Penta-	1496	1505	1525	1552
Hexa-	1656	1673	1695	1723

TABLE II

RETENTION INDICES OF CHLOROBENZENE ISOMERS ON CARBOWAX 20M

Isomer	*Temperature (°C)*			$\frac{I_{CW\ 20M}^{\star}}{I_{SE\text{-}30}}$
	140	*160*	*180*	
	1257	1270	1289	1.51
1,3-Di-	1415	1434	1509	1.41
1,4-Di-	1438	1471	1529	1.44
1,2-Di-	1447	1514	1575	1.44
1,3,5-Tri-	1515	1545	1590	1.34
1,2,4-Tri-	1630	1653	1698	1.39
1,2,3-Tri-	1705	1735	1775	1.41
1,2,3,5-Tetra-	1754	1786	1824	1.33
1,2,4,5-Tetra-	1764	1793	1830	1.33
1,2,3,4-Tetra-	1871	1908	1941	1.37
Penta-	1956	1999	2027	1.31
Hexa-	2124	2178	2204	1.28

* Ratio determined at 160°C; for values on SE-30 see Table I.

The retention behaviour of the isomers on SE-30 also largely follows the behaviour of the acetyl esters of the chlorinated phenols which were reported recently[10].

At lower temperatures, the 1,3-dichloro isomer has a slightly lower retention than the 1,4-dichloro isomer, while the 1,2-dichloro isomer with a vicinal chlorine atoms has the greatest retention. On this basis, the 1,3-dichloro isomer might have been expected to have a greater retention than the 1,4-dichloro isomer. Owing to their similar boiling points (172 and 174°C, respectively), however, the differences are very small, leading to the same retention at higher temperatures.

The trichloro and tetrachloro isomers follow the pattern reported previously for the acetyl esters of chlorinated phenols[10].

The retention on the more polar Carbowax 20M stationary phase is increased as expected, although the elution order is not altered as occurs with several of the chlorophenyl acetate isomers. The elution order is as reported earlier on Carbowax 20M[3,4]. Separation of several isomers that had the same retention on SE-30 is observed, complete resolution of the mixture being achieved at lower temperatures, *i.e.*, 120 and 140°C.

The incremental effect of chlorine addition is shown in Tables III and IV, where it is apparent that with both stationary phases the incremental differences increase with temperature. This is in agreement with the results for chlorophenyl acetate isomers[10], although with the chlorobenzenes the effect is more pronounced.

With chlorophenyl acetates the incremental retention increases tend to be relatively constant with different levels of chlorine substitution and vary rather with the position of substitution, whereas with the chlorobenzenes the incremental increases show a definite increase with the level of chlorine substitution, although the effect is accentuated by the particular positions of substitution. The effect is shown below, where the lowest retention isomers, *i.e.*, 1,3- → 1,3,5- → 1,2,3,5-, at 160°C on SE-30

TABLE III

INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION WITH TEMPERATURE ON SE-30

Chlorobenzene isomer	*Temperature (°C)*							
	120		*140*		*160*		*180*	
	*ΣΔI**	*ΔI***	*ΣΔI**	*ΔI***	*ΣΔI**	*ΔI***	*ΣΔI**	*ΔI***
1,3-Di-	132	66	177	89	176	88	174	87
1,4-Di-	138	69	179	90	176	88	174	87
1,2-Di-	173	87	202	101	210	105	215	108
1,3,5-Tri-	299	100	308	103	310	103	317	106
1,2,4-Tri-	345	115	347	116	353	118	365	122
1,2,3-Tri-	379	126	381	127	388	129	405	135
1,2,3,5-Tetra-	494	124	493	123	504	126	525	131
1,2,4,5-Tetra-	494	124	493	123	504	126	525	131
1,2,3,4-Tetra-	534	134	535	134	548	137	570	143
Penta-	664	133	669	134	685	137	710	142
Hexa-	824	137	837	140	855	143	881	147

* Total retention index increase.

** Retention index increase per chlorine atom.

TABLE IV

INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION WITH TEMPERATURE ON CARBOWAX 20M

Chlorobenzene isomer	*Temperature (°C)*					
	140		*160*		*180*	
	$\Sigma\Delta I$*	ΔI*	$\Sigma\Delta I$*	ΔI*	$\Sigma\Delta I$*	ΔI*
1,3-Di-	158	79	164	82	220	110
1,4-Di-	181	91	201	101	240	120
1,2-Di-	190	95	244	122	286	143
1,3,5-Tri-	258	86	275	92	301	100
1,2,4-Tri-	373	124	383	128	409	136
1,2,3-Tri-	448	149	465	155	486	162
1,2,3,5-Tetra-	497	124	516	129	535	134
1,2,4,5-Tetra-	507	127	523	131	541	135
1,2,3,4-Tetra-	614	154	638	160	652	163
Penta-	699	140	729	146	738	148
Hexa-	867	145	908	151	915	153

* As in Table III.

show retention index increases for the chlorine atom of 91 → 103 → 126 index units (i.u.), whereas the highest retention isomers, i.e., 1,2- → 1,2,3- → 1,2,3,4-, show retention index increases of 105 → 129 → 137 i.u.

The same trend is shown on the Carbowax 20M stationary phase, where the two series are 1,3- → 1,3,5- → 1,2,3,5- = 82 → 92 → 129 i.u. and 1,2- → 1,2,3- → 1,2,3,4- = 122 → 155 → 160 i.u. The position of substitution is obviously of some importance in the operation of the polar solute–solvent interactions with the polar stationary phase with the lowest retention isomers, the relative incremental effect on SE-30 and Carbowax 20M being low. However, with the highest retention isomers the retention increases on Carbowax 20M are significantly increased.

The relative polar and steric effects are indicated by the increments shown in Table III and particularly Table IV, and by retention index ratios on the two columns determined at 160°C as shown in Table II. Although major retention variations due to either effect are not evident, it is clear that the polar effects are maximized with the 1,2,3,4-tetrachloroisomer and with further substitution the polar effects are reduced owing to steric constraints.

ACKNOWLEDGEMENTS

I.O.O.K. expresses his gratitude to the Foundation for Research on Natural Resources in Finland and the Leo and Regina Wainstein Foundation for financial support.

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