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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XXVII*. SEPARATION OF CHLORINATED 4-HYDROXYBENZALDEHYDES ON A CAPILLARY COLUMN COATED WITH NON-POLAR SE-30 STATIONARY PHASE

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SUMMARY

A mixture of all nine chlorinated 4-hydroxybenzaldehydes and the parent homologue was separated on a non-polar SE-30 capillary column using various isothermal and temperature-programmed operating conditions. The relative retention data for the compounds are given and the retention indices together with the retention index increments for each position of chlorine substitution are examined. The retention order 3-Cl < parent < 2,5-di-Cl < 2,3-di-Cl < 3,5-di-Cl < 2-Cl < 2,3,5-tri-Cl < 2,3,6-tri-Cl < 2,6-di-Cl < tetra-Cl isomer obtained indicates that the effect of the position of substitution on the retention behaviour is greater than that of the number of chlorine atoms. The retention is maximal with 2-Cl and 2,6-di-Cl isomers, *i.e.*, *o*-chloro and *o,o'*-dichloro isomers with respect to the formyl group, and minimal with the 3-Cl isomer, *i.e.*, *o*-chloro isomer with respect to the hydroxy group.

INTRODUCTION

The importance¹ of the chlorinated 4-hydroxybenzaldehydes has been increasing owing to their use as substrates in several organic syntheses and to their undesirable presence in effluents from kraft bleaching.

Temperature-programmed gas chromatography (GC) of the acetyl derivatives of all chlorinated 4-hydroxybenzaldehydes on non-polar OV-101 and SE-30 capillary columns has been studied by Knuutinen *et al.*¹, the effects of the number of chlorine atoms and the position of substitution on the retention behaviour of the isomers having been examined by multiple linear regression analysis.

This work extends the earlier GC studies with chlorinated aromatics² by showing the retention behaviour of the chlorinated 4-hydroxybenzaldehydes. The separations were carried out on a non-polar SE-30 capillary column with isothermal and temperature-programmed conditions. The relative retention data and the retention

* For Part XXVI, see I. O. O. Korhonen, *J. Chromatogr.*, 288 (1984) 329.

indices with the retention index increments for each position of substitution are examined and the retention sequence of the isomers is compared with that reported earlier for the acetyl derivatives of chlorinated 4-hydroxybenzaldehydes¹.

EXPERIMENTAL

Materials

4-Hydroxybenzaldehyde was a commercial product (Fluka, Buchs, Switzerland). All chlorinated 4-hydroxybenzaldehydes were prepared and their structures verified in our laboratory as described earlier³.

Commercial mixtures of *n*-alkanes were obtained from different sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 instrument under the following operating conditions: injection and flame-ionization detection (FID) temperatures, 275°C; carrier gas (nitrogen) flow-rate, 1 ml min⁻¹; splitting ratio, 1:50; and chart speed, 10 mm min⁻¹. The column used was a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia). The isothermal data were obtained at 160, 180 and 200°C and the column temperature was programmed from 100°C at 6, 10 and 14°C min⁻¹ until elution of peaks had ceased.

The retention times were measured from the time of sample injection, the dead volume being determined by the injection of methane. The Kováts retention indices were calculated off-line by using two appropriate adjacent *n*-alkanes, as described earlier⁴.

RESULTS AND DISCUSSION

The retention data for the chlorinated 4-hydroxybenzaldehydes and the data for phenol and benzaldehyde are given in Table I, relative to 4-hydroxybenzaldehyde (= 1.00). Table II gives the retention indices for the components, and the incremental effect of chlorine substitution is shown in Tables III and IV and Fig. 2.

The separation of a mixture of the compounds with the structure and notation of 4-hydroxybenzaldehydes is shown in Fig. 1, obtained with a temperature-programmed run. The SE-30 stationary phase used seemed to be unsuitable for the components studied, giving tailing and broadened peaks for some isomers, particularly under isothermal conditions. A capillary column with another non-polar stationary phase might be better for the compounds studied; polar columns are unsuitable for chlorinated phenolic compounds^{5,6}, and have not been used with the isomers studied.

The retention data for phenol and benzaldehyde are shown in Tables I and II, the components being eluted close together owing to their similar boiling points (181.75 and 178.1°C, respectively). Phenol is eluted first under isothermal conditions, whereas the sequence altered with the slowest temperature programming rate used of 6°C min⁻¹. As shown, with higher programming rates the components are coincident. The enhanced retention for 4-hydroxybenzaldehyde, relative to phenol, under various conditions is in the range 356–394 retention index units (i.u.) and relative to benzaldehyde it is in the range 342–389 i.u., as can be seen from Table II.

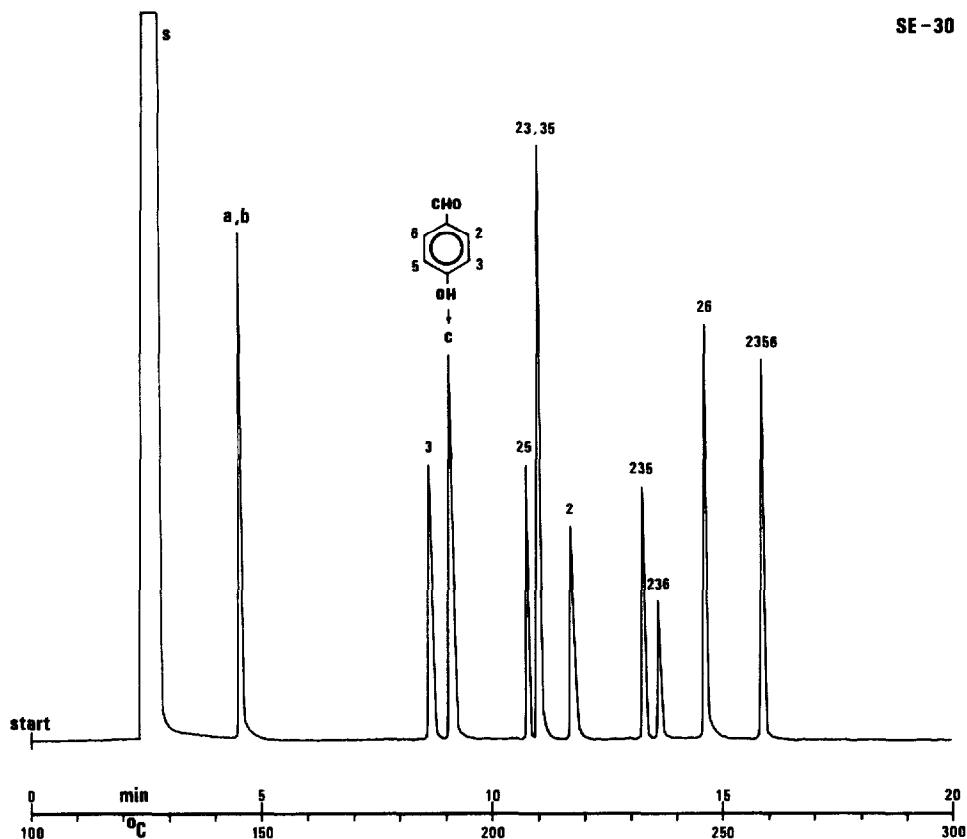


Fig. 1. Chromatogram of a mixture of (a) phenol, (b) benzaldehyde, (c) 4-hydroxybenzaldehyde and its chlorinated derivatives (the numbers indicate the positions of chlorination). S = Solvent. Column (SE-30) temperature programmed from 100°C at 10°C min⁻¹ until elution of peaks had ceased.

The retention order observed for the 4-hydroxybenzaldehydes studied was 3-Cl < parent < 2,5-di-Cl < 2,3-di-Cl < 3,5-di-Cl < 2-Cl < 2,3,5-tri-Cl < 2,3,6-tri-Cl < 2,6-di-Cl < tetra-Cl isomer. The elution sequence remained unaltered under various operating conditions and the retention index generally increased with increasing column temperature. All components are solids³, having unknown and obviously very high boiling points. Hence it is uncertain if the elution sequence observed follows the order of the boiling points, as generally occurs with homologous series on a non-polar column.

The 3-chloro isomer is eluted earlier than the parent component, with a reduction in the retention of 29 i.u. at 160°C (Table III) (the retention indices or retention index increments mentioned later always refer to values obtained at 160°C). The reduction observed is due to the *ortho*-effect between the chlorine atom and the hydroxy group, the same phenomenon having previously been observed with the compound pair catechol (1,2-dihydroxybenzene) and 3-chlorocatechol, separated on SE-30⁵. Phenol, however, in spite of its about 6°C higher boiling point, appeared earlier than 2-chlorophenol from SE-30^{5,6}.

TABLE I
RETENTION DATA FOR PHENOL, BENZALDEHYDE AND 4-HYDROXYBENZALDEHYDES, DETERMINED ON SE-30 UNDER VARIOUS CONDITIONS

Compound	Column temperature																	
	Isothermal			Programmed from 100°C														
	160°C			180°C			200°C			6°C min ⁻¹			10°C min ⁻¹			14°C min ⁻¹		
	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**	ART*	RRT**
Phenol	3.43	0.51	3.19	0.64	3.06	0.73	4.92	0.42	4.48	0.49	4.23	0.55						
Benzaldehyde	3.49	0.52	3.22	0.65	3.10	0.74	4.87	0.42	4.48	0.49	4.23	0.55						
4-Hydroxybenzaldehyde	6.70	1.00	4.98	1.00	4.17	1.00	11.71	1.00	9.09	1.00	7.76	1.00						
2-Chloro-4-hydroxybenzaldehyde	12.47	1.86	7.79	1.56	5.72	1.37	15.95	1.36	11.71	1.29	9.82	1.27						
3-Chloro-4-hydroxybenzaldehyde	6.23	0.93	4.83	0.97	4.12	0.99	10.79	0.92	8.64	0.95	7.41	0.95						
2,3-Dichloro-4-hydroxybenzaldehyde	10.20	1.52	6.95	1.29	5.38	1.29	14.58	1.25	10.99	1.21	9.31	1.20						
2,5-Dichloro-4-hydroxybenzaldehyde	9.74	1.45	6.69	1.34	5.24	1.26	14.19	1.21	10.75	1.18	9.14	1.18						
2,6-Dichloro-4-hydroxybenzaldehyde	29.14	4.35	15.34	3.08	9.48	2.27	20.51	1.75	14.61	1.61	11.98	1.54						
3,5-Dichloro-4-hydroxybenzaldehyde	10.25	1.53	6.97	1.40	5.38	1.29	14.62	1.25	10.99	1.21	9.31	1.20						
2,3,5-Trichloro-4-hydroxybenzaldehyde	18.31	2.73	11.02	2.21	7.61	1.82	18.24	1.56	13.27	1.46	11.07	1.43						
2,3,6-Trichloro-4-hydroxybenzaldehyde	19.66	2.93	11.70	2.35	7.96	1.91	18.81	1.61	13.60	1.50	11.30	1.46						
Tetrachloro-4-hydroxybenzaldehyde	37.99	5.67	20.52	4.12	12.46	2.99	22.30	1.90	15.87	1.75	12.92	1.66						

* Absolute retention times (min) were measured from sample injection (e.g., Fig. 1).

** Relative retention time for 4-hydroxybenzaldehyde taken as 1.00.

TABLE II
RETENTION INDICES FOR THE COMPOUNDS STUDIED AT VARIOUS COLUMN TEMPERATURES

Compound	Column (SE-30) temperature					
	Isothermal			Programmed from 100°C		
	160°C	180°C	200°C	6°C min ⁻¹	10°C min ⁻¹	14°C min ⁻¹
Phenol	964	924	—	933	942	933
Benzaldehyde	978	941	—	929	942	933
4-Hydroxybenzaldehyde	1320	1318	1302	1318	1324	1308
2-Chloro-4-hydroxybenzaldehyde	1524	1520	1514	1523	1523	1516
3-Chloro-4-hydroxybenzaldehyde	1291	1301	1291	1274	1290	1275
2,3-Dichloro-4-hydroxybenzaldehyde	1463	1474	1479	1455	1467	1463
2,5-Dichloro-4-hydroxybenzaldehyde	1449	1459	1464	1435	1449	1445
2,6-Dichloro-4-hydroxybenzaldehyde	1753	1750	1749	1754	1754	1755
3,5-Dichloro-4-hydroxybenzaldehyde	1465	1476	1479	1457	1467	1463
2,3,5-Trichloro-4-hydroxybenzaldehyde	1632	1644	1655	1636	1646	1652
2,3,6-Trichloro-4-hydroxybenzaldehyde	1651	1664	1675	1665	1672	1678
Tetrachloro-4-hydroxybenzaldehyde	1820	1839	1856	1852	1864	1867

2-Chloro-4-hydroxybenzaldehyde, in which the chlorine atom is adjacent to the formyl group, showed a high enhancement of the retention, *i.e.*, 204 i.u. The isomer was eluted even later than most dichloro isomers (Fig. 1). Obviously the relatively high retention time is due to the intramolecular hydrogen bonding between the formyl proton and the adjacent chlorine substituent⁷. Hence, the free rotation of the formyl group would be hindered, causing an increased retention. Such an effect is greater on polar columns and the use of a suitable polar column might have confirmed the assumption mentioned, but such a column was not available.

The di- and polychloro isomers generally follow the pattern of the monochloro isomers, *i.e.*, the isomers with a chlorine atom substitution adjacent to the hydroxy group are eluted first. A second chlorine atom introduced into the 3- or 5-position of the 2-chloro isomer, *i.e.*, giving the *ortho*-effect, seems to compensate for the interaction between the formyl group and the chlorine atom, the reduction observed in the retention of the 2,3- and 2,5-dichloro isomers being 61 and 75 i.u., respectively, relative to the 2-chloro isomer (Table IV). As would be expected, the "symmetrical" 2,5-dichloro isomer was eluted first, and thereafter the 2,3- and 3,5-dichloro isomers appeared close together, becoming completely overlapped with increasing column temperature. The retention enhancement for the 3,5-dichloro isomer, relative to the 3-chloro isomer, is relatively high, *i.e.*, 174 i.u. (Table IV), owing to the canceled *ortho*-effect of the competitive chlorine atoms. The 2,6-dichloro isomer, as expected, is eluted last, even later than the trichloro isomers. The retention enhancement, with respect to the 2-chloro isomer, is 229 i.u., the retention index increase per chlorine atom being 217 i.u., *i.e.*, 13 i.u. higher than with the 2-chloro isomer (Fig. 2).

As a consequence of the retention behaviour of the dichloro isomers, the 2,3,5-trichloro isomer is eluted earlier than the 2,3,6-trichloro isomer, the tetrachloro isomer being eluted last. As is evident from Tables III and IV, the retention increment increases with the 3,5-dichloro → 2,3,5-trichloro isomers from 145 to 312 i.u., *i.e.*,

TABLE III
 INCREMENTAL EFFECT OF CHLORINE SUBSTITUTION AT VARIOUS COLUMN TEMPERATURES

	Column (SE-30) temperature												
	Isothermal				Programmed from 100°C								
	160°C	180°C	200°C	200°C	6°C min ⁻¹	10°C min ⁻¹	10°C min ⁻¹	14°C min ⁻¹	14°C min ⁻¹	14°C min ⁻¹	14°C min ⁻¹	14°C min ⁻¹	
$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$	$\Sigma\Delta I_{\text{HCl}}^*$	$\Delta I_{\text{HCl}}^{**}$
2-Cl	204	204	202	212	205	205	205	205	205	199	199	208	208
3-Cl	-29	-29	-17	-11	-44	-44	-44	-44	-44	-34	-34	-33	-33
2,3-Di-Cl	143	72	156	89	137	137	69	143	72	155	155	78	78
2,5-Di-Cl	129	65	141	81	117	117	59	125	63	137	137	69	69
2,6-Di-Cl	433	217	432	224	436	436	218	430	215	447	447	224	224
3,5-Di-Cl	145	73	158	89	139	139	70	143	72	155	155	78	78
2,3,5-Tri-Cl	312	104	326	118	318	318	106	322	107	344	344	115	115
2,3,6-Tri-Cl	331	110	346	124	347	347	116	348	116	370	370	123	123
Tetra-Cl	500	125	521	139	534	534	134	540	135	559	559	140	140

* Total retention index increase.

** Retention index increase per chlorine atom.

TABLE IV
 INCREMENTAL EFFECT OF AN ADDITIONAL CHLORINE ATOM INTRODUCED INTO 4-HYDROXYBENZALDEHYDE AND ITS CHLORINATED DERIVATIVES, OBTAINED ON SE-30 AT 160°C

Lower isomer with nCl, n = 0-3	Higher isomer with (n+1)Cl, n = 0-3																		
	2-Cl		3-Cl		2,3-Di-Cl		2,5-Di-Cl		2,6-Di-Cl		3,5-Di-Cl		2,3,5-Tri-Cl		2,3,6-Tri-Cl		Tetra-Cl		
	$\Sigma \Delta I^*$	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^{**}	
Parent	204	204	-29	-29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Cl	-	-	-	-	-61	-132	-75	-139	229	13	-	-	-	-	-	-	-	-	-
3-Cl	-	-	-	-	172	101	158	94	-	-	174	102	-	-	-	-	-	-	-
2,3-Di-Cl	-	-	-	-	-	-	-	-	-	-	-	-	169	32	188	38	-	-	-
2,5-Di-Cl	-	-	-	-	-	-	-	-	-	-	-	-	183	39	202	45	-	-	-
2,6-Di-Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-102	-107	-	-	-
3,5-Di-Cl	-	-	-	-	-	-	-	-	-	-	-	-	167	31	-	-	-	-	-
2,3,5-Tri-Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	188	21	-
2,3,6-Tri-Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	169	15

* Total retention index increase due to an additional chlorine atom, i.e., $\Sigma \Delta I = \Delta I_{(n+1)Cl} - \Delta I_{nCl}$.

** Retention index increase per chlorine atom.

167 i.u., whereas the 2,6-dichloro \rightarrow 2,3,6-trichloro isomers show a reduction in retention from 433 to 331 i.u., *i.e.*, 102 i.u. Hence, the trichloro isomers are eluted close together with a disparity of 19 i.u. at 160°C. The tetrachloro isomer shows enhancements of 188 and 169 i.u., relative to the trichloro isomers (Table IV).

The incremental effect of a chlorine atom generally (*i.e.*, except for the 2-chloro and 2,6-dichloro isomers) increases with increasing the degree of chlorination (Fig. 2) and the incremental differences increase with increasing temperature (Table III), the effect being more pronounced under isothermal than temperature-programmed conditions.

Previous studies with the acetyl derivatives of 4-hydroxybenzaldehydes show the different elution sequences of the isomers on non-polar columns than were found for the free isomers in this work, *i.e.*, parent < 3-Cl < 2-Cl < 3,5-di-Cl < 2,5-di-

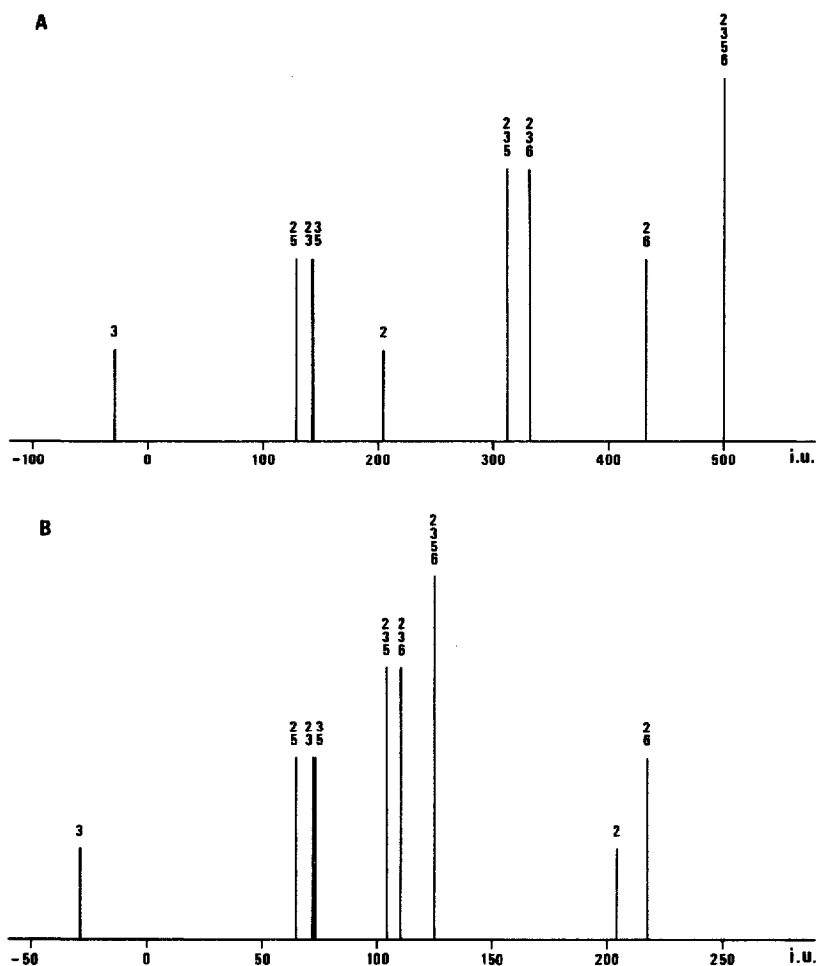


Fig. 2. Incremental effect of chlorine substitution, obtained on SE-30 at 160°C. A = Total retention index increase; B = retention index increase per chlorine atom; i.u. = retention index units; the numbers indicate the positions of chlorination.

Cl < 2,3-di-Cl < 2,6-di-Cl < 2,3,5-tri-Cl < 2,3,6-tri-Cl < tetra-Cl isomer¹. As shown, the acetyl derivatives are eluted in order of increasing degree of chlorination; on the other hand, the retention order between the dichloro isomers is altered, *i.e.*, the 3,5-dichloro isomer is eluted first. In contrast to the present work, the most important effect on the retention behaviour of the acetyl derivatives is the number of chlorine atoms, the effect of the position of chlorine substitution being smaller¹.

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