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Note

Gas–liquid chromatographic analyses

XL*. Incremental effects of a formyl group introduced into the *ortho*- and *para*-positions of isomeric chlorophenols

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The gas chromatographic (GC) retention behaviour of various groups of chlorinated aromatics on both low-polarity and polar capillary columns has been reported previously[1]. Temperature programming has been used to optimize the separation of the individual isomers in complex mixtures, whereas the retention indices and the retention index increments for each position of substitution, together with the effect of increasing temperature on the values, have been examined and discussed most frequently based on isothermal data. More recently, the retention enhancements of hydroxy, methoxy and acetoxy groups introduced into various non-chlorinated and chlorinated positions of isomeric chlorobenzenes[2] and the corresponding effects due to the *o*-chloro and *o*-methoxy substitution in isomeric chloroanisoles[3] have been investigated on both low-polarity and polar capillary columns.

This paper extends the earlier studies on the GC retention behaviour of chlorinated phenols[4], 2-hydroxybenzaldehydes[1] and 4-hydroxybenzaldehydes[5] by showing the retention enhancements that occurred on low-polarity (SE-30) and polar (OV-351) capillary columns owing to the introduction of a formyl group into the *o*- and *p*-positions of isomeric chlorophenols. The effects of Cl and CHO ring substituents at various positions are compared and discussed and the effect of the polarity of the stationary phase on the retention increments is examined.

EXPERIMENTAL

Samples

Phenol, all chlorophenols, 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde were commercial products (Fluka, Buchs, Switzerland). Chlorinated 2-hydroxybenzaldehydes were prepared from chlorophenols by the Reimer–Tiemann method[6] and chlorinated 4-hydroxybenzaldehydes were synthesized as described earlier[7].

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

* For Part XXXIX, see I. O. O. Korhonen, *J. Chromatogr.*, 324 (1985) 181.

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Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the operating conditions reported earlier[1,4,5]. The columns used were a low-polarity SE-30 vitreous-silica wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia), a polar FFAP vitreous-silica WCOT column (25 m × 0.35 mm I.D.), supplied by SGE, and a polar OV-351 fused-silica WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The FFAP stationary phase was used with chlorophenols and OV-351 with 2- and 4-hydroxybenzaldehydes, these two polar phases having been shown to be almost identical for the separation of chlorophenol isomers[8].

The data presented were obtained isothermally at 160°C and the retention indices were calculated as described earlier[1,4,5].

RESULTS AND DISCUSSION

The retention increments for a formyl group, introduced into the *o*- and *p*-positions of phenol and chlorophenols, obtained on SE-30 and OV-351 at 160°C are given in Table I, which also shows the incremental effects due to the replacement of an *o*- and *p*-chlorine atom in isomeric chlorophenols with a formyl group. Fig. 1 shows the retention increments for 2-hydroxybenzaldehydes and Fig. 2 those for 4-hydroxybenzaldehydes. A summary of the incremental effects is presented in Table II, and Table III compares the increments of 2- and 4-hydroxybenzaldehydes, originating from the same phenol isomer, on SE-30.

As would be expected, an additional *o*-formyl group in phenols generally causes a retention enhancement on a low-polarity stationary phase, owing to an increase in the molecular weight, whereas on a polar column, which is much more influenced by the structures of the components, a reduction in the retention is most frequently observed (Fig. 1a).

The retention of the parent isomer (2-hydroxybenzaldehyde) is increased by 133 retention index units (i.u.) on SE-30, but decreased by −258 i.u. on OV-351. A formyl group introduced into *o*-chlorophenols always causes an enhanced retention owing to the *ortho*-effect in phenols, *i.e.*, *o*-chlorophenols show lower retentions than the other isomers[4]. Table II indicates that the increments fall into two groups, *viz.*, on introduction of a formyl group into (i) the geminal *o*-position, 214–273 i.u. on SE-30 and 163–266 i.u. on OV-351, and (ii) the vicinal *o*-position, 166–217 i.u. on SE-30 and 0 i.u. on OV-351 (only one isomer among the mono- and dichloro isomers investigated on a polar column, *i.e.*, 2,5-dichlorophenol, is included in this group). An additional *o*-formyl group in *m*- and *p*-chlorophenols, which have higher retentions than the *o*-isomers[4], gives a minimal increase or decrease in the retention on SE-30, *i.e.*, from −77 to 57 i.u., whereas the reductions observed in the retentions on OV-351 are dramatic, *viz.*, from −718 to −405 i.u. (Table II and Fig. 1a). The position of the formyl group (geminal or vicinal with respect to a chlorine atom) seems to have a negligible effect on the incremental effects (Table I) and the increments lie in the same ranges with both substituted *m*- and *p*-chlorophenols (Table II).

The effects due to the replacement of an *o*-chlorine atom in chlorophenols with a formyl group, *i.e.*, the difference between the Cl and CHO ring substituents in

TABLE I

RETENTION INCREMENTS* FOR A FORMYL GROUP, INTRODUCED (→) INTO THE *o*- AND *p*-POSITIONS OF PHENOL AND CHLOROPHENOLS AND THE INCREMENTAL EFFECTS DUE TO THE REPLACEMENT (➡) OF AN *o*- AND *p*-CHLORINE ATOM IN ISOMERIC CHLOROPHENOLS WITH A FORMYL GROUP

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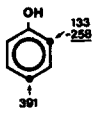	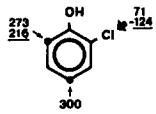	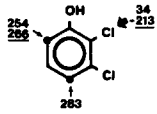	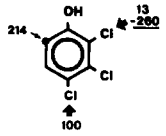	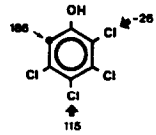	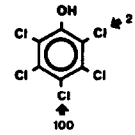
	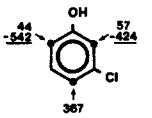	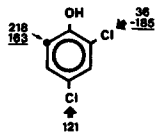	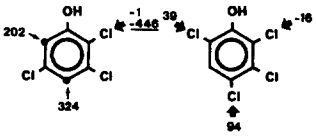		
	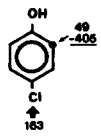	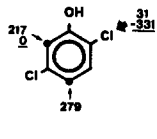	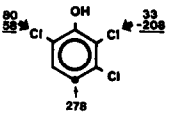	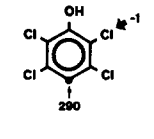	
		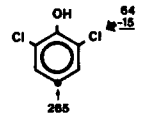	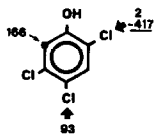		
		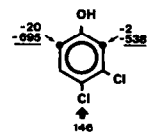	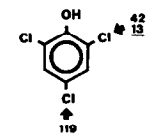		
		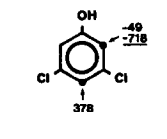	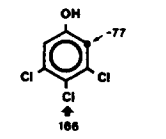		

* Increments were obtained on low-polarity (SE-30) and polar (OV-351) capillary columns at 160°C. The upper or single values were obtained on SE-30 and the lower, underlined values on OV-351.

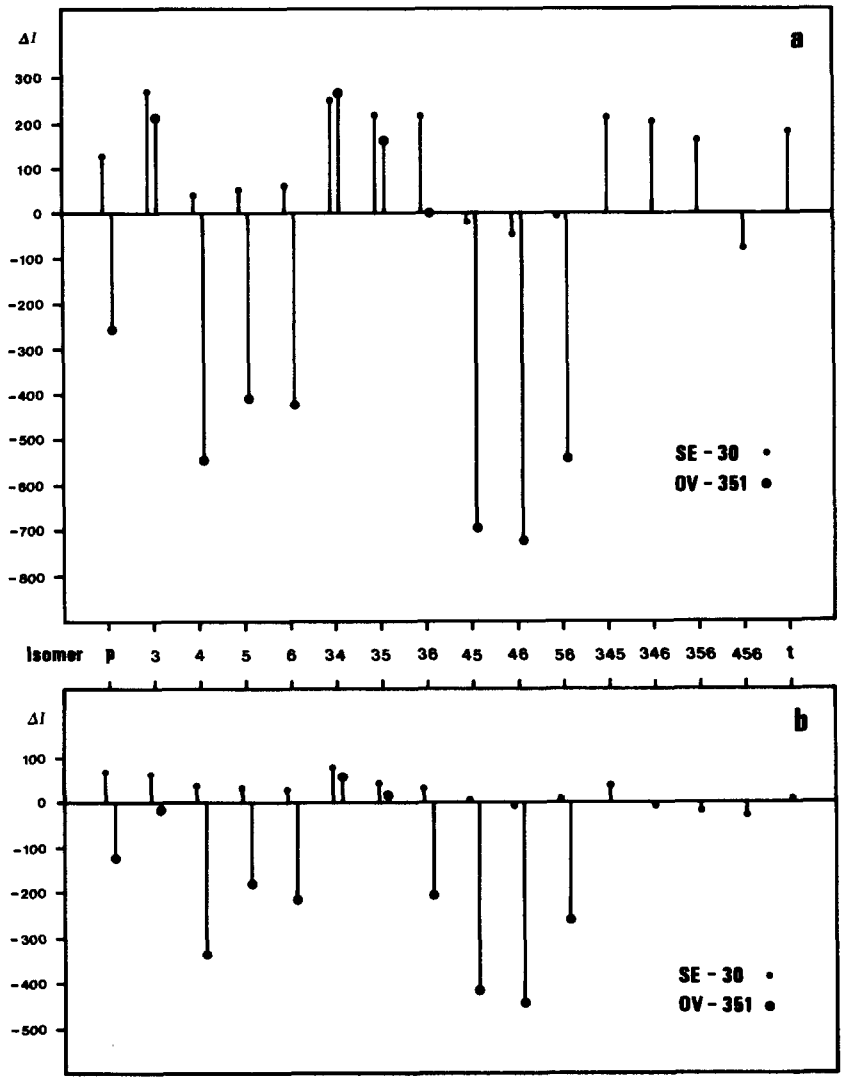

Fig. 1. (a) Incremental effects due to an additional formyl group introduced into the non-chlorinated *o*-positions of isomeric chlorophenols. ΔI (i.u.) = $I_{\text{nCl 2-hydroxybenzaldehyde}} - I_{\text{nCl phenol}}$. (b) Incremental effects due to the replacement of an *o*-chlorine atom in chlorophenols with a formyl group. ΔI (i.u.) = $I_{\text{(n-1)Cl 2-hydroxybenzaldehyde}} - I_{\text{nCl phenol}}$. Increments were obtained on SE-30 and OV-351 at 160°C (Table I). The numbers of the isomers indicate the positions of chlorination: p = the parent isomer (2-hydroxybenzaldehyde); t = the tetrachloro isomer.

isomeric phenols, presented in Table I and Fig. 1b, are less prominent, as stated above. On SE-30 this is, of course, due to a decrease in the molecular weight, whereas on OV-351 such a decrease has a negligible effect, unlike to the nature and position of the substituents.

Replacement of a geminal *o*-chlorine atom with a formyl group causes retention enhancements of 2–80 and from −417 to 58 i.u. on SE-30 and OV-351, respec-

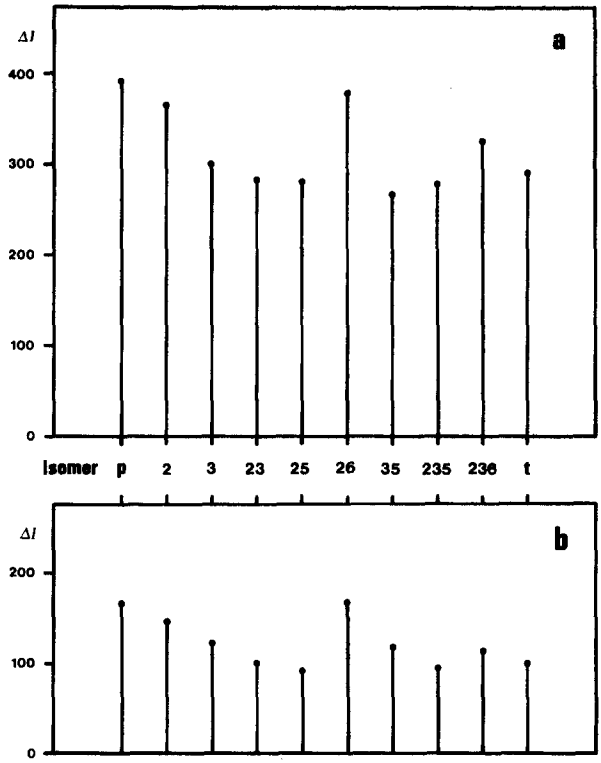

Fig. 2. (a) Incremental effects due to an additional formyl group introduced into the non-chlorinated *p*-positions of isomeric chlorophenols. ΔI (i.u.) = $I_{nCl\ 4\text{-hydroxybenzaldehyde}} - I_{nCl\ phenol}$. (b) Incremental effects due to the replacement of a *p*-chlorine atom in chlorophenols with a formyl group. ΔI (i.u.) = $I_{(n-1)Cl\ 4\text{-hydroxybenzaldehyde}} - I_{nCl\ phenol}$. Increments were obtained on SE-30 at 160°C (Table I). The numbers of the isomers indicate the positions of chlorination; p = the parent isomer (4-hydroxybenzaldehyde); t = the tetrachloro isomer.

tively. Replacement of a vicinal *o*-chlorine atom gives rise to lower increments, *i.e.*, from −26 to 34 i.u. on SE-30 and from −446 to −208 i.u. on OV-351 (Table II). The greatest differences between the chlorine and formyl substituents on SE-30 are shown by 2,3,4,5-tetrachlorophenol → 4,5,6-trichloro-2-hydroxybenzaldehyde (−26 i.u.) and 2,3,6-trichlorophenol → 3,4-dichloro-2-hydroxybenzaldehyde (80 i.u.) and on OV-351 by 2,3,5-trichlorophenol → 4,6-dichloro-2-hydroxybenzaldehyde (−446 i.u.) and 2,3,6-trichlorophenol → 3,4-dichloro-2-hydroxybenzaldehyde (58 i.u.), as is evident from Table I and Fig. 1b.

The data for 4-hydroxybenzaldehydes are available only on a low-polarity SE-30 capillary column, shown in Tables I and II and Fig. 2. As is evident, the retention increments observed are higher than those with the 2-hydroxy isomers and the increments are always positive. The effects with various isomers are fairly constant, *i.e.*, with replacement of a hydrogen and chlorine atom in the ranges 265–391 and 93–166 i.u., respectively (Fig. 2 and Table II).

A comparison between the incremental effects of 2- and 4-hydroxybenzaldehydes, originating from the same chlorophenol isomers, is shown in Table III. An

TABLE II

SUMMARY OF THE INCREMENTAL EFFECTS PRESENTED IN TABLE I

Formyl group	*Stationary phase*	
	SE-30	*OV-351*
	*ΔI**	*ΔI**
Introduced into the *o*-position of:		
Phenol	133	−258
o-Chlorophenol (geminal position**)	214–273	163–266
o-Chlorophenol (vicinal position**)	166–217	0
m-Chlorophenol	−77 to 57	−718 to −424
p-Chlorophenol	−77 to 49	−695 to −405
Introduced into the *p*-position of:		
Phenol	391	
o-Chlorophenol	265–324	
m-Chlorophenol	367, 378	
Substitution in chlorophenols of:		
Geminal *o*-chlorine atom	2–80	−417 to 58
Vicinal *o*-chlorine atom	− 26 to 34	−446 to −208
p-Chlorine atom	93–166	

* $\Delta I = I_{\text{isomer formed}} - I_{\text{phenol substituted}}$.
** With respect to a chlorine atom.

TABLE III

COMPARISON BETWEEN THE INCREMENTAL EFFECTS OF 2- AND 4-HYDROXYBENZALDEHYDES ON SE-30, OBTAINED BY INTRODUCING A FORMYL GROUP INTO THE *o*- AND *p*-POSITIONS OF THE SAME PHENOL ISOMER

*Phenol isomer substituted**	*2-Hydroxybenzaldehyde*		*4-Hydroxybenzaldehyde*		$\Delta I_{4\text{-OH}} - \Delta I_{2\text{-OH}}$
	*Isomer formed**	$\Delta I_{2\text{-OH}}$**	*Isomer formed**	$\Delta I_{4\text{-OH}}$**	
H substitution:					
Parent	Parent	133	Parent	391	258
2-	3-	273	3-	300	27
3-	4-	44	2-	367	323
3-	6-	57	2-	367	310
2,3-	3,4-	254	2,3-	283	29
2,5-	3,6-	217	2,5-	279	62
3,5-	4,6-	−49	2,6-	378	427
2,3,5-	3,4,6-	202	2,3,6-	324	122
Cl substitution:					
2,4-	5-	36	3-	121	85
2,3,4-	5,6-	13	2,3-	100	87
2,4,5-	4,5-	2	2,5-	93	91
2,4,6-	3,5-	42	3,5-	119	77
2,3,4,5-	4,5,6-	−26	2,3,6-	115	141
2,3,4,6-	3,4,5-	39	2,3,5-	94	55
2,3,4,6-	3,5,6-	−16	2,3,5-	94	110
2,3,4,5,6-	3,4,5,6-	2	3,4,5,6-	100	98

* The numbers of the isomers indicate the positions of chlorination.
** $\Delta I_{2\text{-OH}} = I_{\text{2-hydroxybenzaldehyde}} - I_{\text{phenol}}$.
*** $\Delta I_{4\text{-OH}} = I_{\text{4-hydroxybenzaldehyde}} - I_{\text{phenol}}$.

additional formyl group introduced into the *o*- and *p*-positions of 2-chloro- and 2,3-dichlorophenol shows the smallest differences of 27 and 29 i.u., respectively, the difference being the greatest with 3,5-dichlorophenol (427 i.u.). Replacement of a chlorine atom with a formyl group in 2,3,4,6-tetrachlorophenol causes the minimum (55 i.u.) and in 2,3,4,5-tetrachlorophenol the maximum difference (141 i.u.) between the 4- and 2-hydroxy isomers.

The effects of the introduction of an additional chlorine atom into various positions of isomeric phenols and 2- and 4-hydroxybenzaldehydes have been reported previously[1,4,5] and the possible influences on the retention behaviour of the isomeric compounds have been examined and discussed, explaining to a certain extent the phenomena observed in this work.

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