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STRUCTURE–RETENTION CORRELATIONS OF ALKYLPHENOLS IN GAS–LIQUID AND GAS–SOLID CHROMATOGRAPHY

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SUMMARY

The retention behaviour of alkyl- and dialkylphenols has been investigated by gas–liquid chromatography (GLC) on glass capillary columns, coated with PS-255 and OV-1701-Vi, and by gas–solid chromatography (GSC) on a microcolumn, packed with uncoated graphitized thermal carbon black (GTCB). The dependence of the chromatographic properties of the alkyl phenols on their molecular structure is discussed. Due to electronic and steric effects, alkyl groups neighbouring the phenolic hydroxyl group decrease the retention values in GLC. In contrast, the interaction between vicinal alkyl groups leads to increased retention. GSC on GTCB is advantageous for the distinction of *meta*- and *para*-isomers, which are difficult to separate by GLC.

INTRODUCTION

Alkylphenols are compounds with very wide industrial application, and their analysis is practical problem[1–3]. Gas chromatographic (GC) investigation of complex alkylphenol mixtures is difficult due to the high solute polarity, low separation selectivity of isomeric compounds with similar properties, the lack of standards and the similarity of mass spectra of isomeric alkylphenols. One way to overcome these difficulties is to use capillary columns that exhibit high interness, high efficiency, high thermostability and suitable polarity. The use of well deactivated capillary columns enables the elution of underivatized alkylphenols without tailing, even on non-polar stationary phases. On the other hand, the use of gas–solid chromatographic (GSC) columns packed with graphitized thermal carbon black (GTCB) offers an high separation selectivity with respect to the geometrical structure of the substituted phenols.

The utilization of retention data and the knowledge of structure–retention correlations should give information supplementary to GC–mass spectrometry (MS) results for the identification of individual components. However, few Kováts retention indices for alkylphenols on stationary phases of different polarities have been published[3–7]. Therefore, we have investigated the retention behaviour of underivatized C_7 and C_8 alkylphenols on glass capillary columns, coated with PS-255 methylsili-

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cone or with OV-1701-Vi (methyl, phenyl, cyanopropylsilicone) and on a micro column, packed with uncoated GTCB particles.

The influence of the molecular structure of alkylphenols on their chromatographic retention will be discussed on the basis of retention indices and retention index increments. A scheme for calculating retention indices by summation of increments corresponding to individual molecular fragments will be proposed.

EXPERIMENTAL

The gas–liquid chromatographic (GLC) measurements were performed on a Model HP 5890 gas chromatograph, equipped with a flame ionization detector and a Model HP 3393 A computer integrator (Hewlett-Packard, Palo Alto, CA, U.S.A.). The following laboratory-made open-tubular capillary columns were used: (1) 50 m × 0.3 mm I.D., soda glass, deactivated by high-temperature silylation with hexamethyldisilazane[8,9], statically coated with methylsilicone (2% vinyl groups) PS-255, cross-linked with 0.5% dicumyl peroxide[10], film thickness 0.25 μm, (2) 50 m × 0.28 mm I.D., soda glass, deactivated by high-temperature silylation with a mixture of hexamethyl-, diphenyltetramethyl- and divinyltetramethyldisilazane[11,12], statically coated with polysiloxane phase OV-1701-Vi (7% phenyl, 7% cyanopropyl, 1% vinyl groups), cross-linked[10–12], film thickness 0.19 μm.

For the GSC measurements, a Sigma 3B gas chromatograph with a Sigma 10 data station (Perkin-Elmer, Norwalk, CT, U.S.A.) was used. The microcolumn (0.9 m × 2 mm I.D., glass) was packed with GTCB Sterling-MT 3000 (Phase Separations, Solingen, F.R.G.), particle size 0.25–0.50 mm, specific surface area 7.6 m^2/g, according to ref. 13.

The gas hold-up time was estimated by extrapolation from the retention times of *n*-alkanes which were added to the mixture. The Kováts retention indices given in Table I are the arithmetic means of at least four measurements for each compound. The standard deviation of the retention index determination was ± 0.5 index units (I.U.) in the case of capillary columns, and ± 1.5 I.U. in the case of the microcolumn. The GLC retention indices were determined at 150°C, those for GSC at 220°C.

RESULTS AND DISCUSSION

The retention indices of underivatized phenol, alkyl- and dialkylphenols, determined on PS-255, OV-1701-Vi and GTCB are listed, together with ΔI increments, in Table I.

Further GLC investigations on SE-54 polysiloxane and on polyethylene glycol Carbowax 20M will not be discussed in detail in this paper. We found that the retention indices on SE-54 were similar to those obtained on PS-255 except that they were always nearly 35 I.U. higher on the weak polar stationary phase. Furthermore, we could not determine reliable retention index values on Carbowax 20M, because they were not reproducible. GSC on GTCB is advantageous for the distinction between *meta*- and *para*-isomers, which are difficult to separate by GLC.

In order to discuss the dependence of retention on the position, carbon number and shape of the alkyl substituents, the following index increments were calculated for isomeric alkylphenols

$$\partial I_{R} = I_{PR} - I_{P}$$

$$\partial \Delta I_{R} = \Delta I_{PR} - \Delta I_{P}$$

for homologous alkylphenols

$$\partial I_{CH_2} = I_{P(CH_2)_nH} - I_{P(CH_2)_{n-1}H}$$

where I is the retention index of a compound, ΔI the retention index difference between the polar and non-polar column, $\Delta I = I^{OV} - I^{PS}$, R = alkyl group, P = phenol, PR = alkylphenol, $P(CH_2)_nH$, $P(CH_2)_{n-1}H$ are successive members of homologous series of alkylphenols.

Monoalkylphenols

In investigating the retention behaviour of monoalkylphenols, we must distin-

TABLE I

RETENTION INDICES OF ALKYLPHENOLS ON PS-255, I^{PS}, ON OV-1701-Vi, I^{OV}, AT 150°C AND ON GRAPHITIZED THERMAL CARBON BLACK, I^{GTCB}, AT 220°C, AND RETENTION INDEX DIFFERENCES, ΔI^{OV-PS}

Compound	*GLC*			*GSC*
	I^{PS}	I^{OV}	ΔI^{OV-PS}	I^{GTCB}
Phenol	952	1221	269	713
2-Methyl-	1030	1274	244	824
3-Methyl-	1050	1312	262	832
4-Methyl-	1049	1310	261	839
2-Ethyl-	1115	1351	236	888
3-Ethyl-	1143	1407	263	899
4-Ethyl-	1142	1401	259	920
2-*n*-Propyl-	1198	1430	232	964
3-*n*-Propyl-	1236	1493	257	990
4-*n*-Propyl-	1235	1496	261	997*
2-Isopropyl-	1175	1408	233	911
3-Isopropyl-	1207	1463	256	942
4-Isopropyl-	1204	1462	258	949
2-*n*-Butyl-	1299	1530	231	1058
4-*n*-Butyl-	1335	1596	261	1094
2-*sec.*-Butyl-	–	–	–	960
4-*sec.*-Butyl-	1293	1547	254	1002
2-*tert.*-Butyl-	1250	1477	227	942*
4-*tert.*-Butyl-	1274	1530	256	990*
2,3-Dimethyl-	1159	1401	242	977**
2,4-Dimethyl-	1128	1359	231	977**
2,5-Dimethyl-	1130	1360	230	976**
2,6-Dimethyl-	1096	1299	203	957**
3,4-Dimethyl-	1172	1432	260	991**
3,5-Dimethyl-	1146	1399	253	978**

* At 210°C.
** At 150°C.

guish positional isomers and homologous compounds. Among the positional isomers (*ortho-*, *meta-*, and *para-*) the retention increases in the orders:

GLC: *ortho* < *para* < *meta*
GSC: *ortho* < *meta* < *para*

The index differences between *para-* and *meta-*isomers in GLC are very small, even on the polar stationary phases. The elution order is in accord with previously published data[3,6,7].

The retention of the side-chain isomers in GLC and GSC increases in the orders:

propyl substituents: *iso* < *n*
butyl substituents: tertiary < secondary < *n*.

This behaviour is in accord with that of the isomeric alkylbenzenes[14,15]. In GLC, it is attributed to the increased boiling points and to the possibility of hyperconjugation between the alkyl group and the phenolic nucleus, which is higher for *n*-alkyl substitution than for branched isomers. On GTCB, the adsorbent surface is fixed, and the adsorption of phenol molecules on this surface depends mainly on their geometrical structures.

The relationship between ∂I_{CH_2} and carbon number in the alkyl chain of homologous alkylphenols (Fig. 1a–c) is not linear in the case of the lower alkyl substituents. Beginning from four carbon atoms in the alkyl chain, the values increase by 100 I.U. This behaviour is comparable with that of the alkylbenzenes[14]. Takács[16] attributes it to several bond contributions to the retention index, which are only constant if there are at least five carbon atoms in the alkyl chains.

The non-linearity of the increase in the retention index for the first members of homologous alkylphenols must also be explained by electronic and steric effects, induced especially by *ortho*-substitution. In GLC the retention indices of the first members of the *o*-alkylphenols show greater deviation from linearity, because the dispersive interactions between the phenolic hydroxyl group and the stationary phase are sterically more hindered. The longer the alkyl chain, the stronger its dispersive interactions are and, hence, the higher the retention indices.

As expected, the retention behaviours of alkylphenols and alkylbenzenes in GSC are similar because retention depends mainly on the geometric structure.

Dialkylphenols

The retention of the dimethylphenols investigated increases in the orders:

GLC: $2,6 < 2,4 \leqslant 2,5 < 3,5 < 2,3 < 3,4$
GSC: $2,6 < 2,4 < 2,5 < 2,3 < 3,5 < 3,4$

Due to the electronic and steric effects of the alkyl group and the hydroxyl group, discussed above, alkyl groups neighbouring the phenolic hydroxyl group decrease the retention values in GLC ("*ortho* effect"). Obviously, the decrease depends on the size and on the shape of the alkyl groups in *ortho*-position. In the case of 2,6-dialkyl substitution with large groups, the retention decreases considerably.

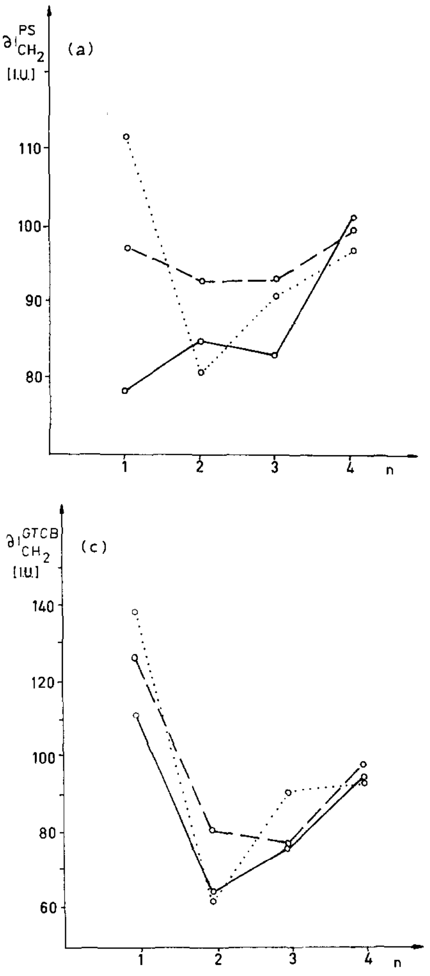

Fig. 1. Relationship between ∂I_{CH_2} increments on (a) PS-255, (b) OV-1701-Vi and (c) GTCB and the carbon number, *n*, of the alkyl chain. ———, *o*-Alkylphenols; --------, *p*-alkylphenols; ...., alkylbenzenes.

Generally, the contribution to retention of the polar intermolecular interactions between the stationary phase and the solute, represented by the ΔI increment (see Table I), increases as the polarity of the stationary phase is increased. However, the ability of the hydroxyl group to interact is low, because it is sterically hindered by the neighbouring alkyl groups. Therefore all 2,6-dialkylphenols are eluted relatively early, especially from polar stationary phases. Thus, 2,6-dimethylphenol is eluted more rapidly than phenol from Carbowax 20M.

In contrast, the interaction between vicinal alkyl groups is reflected as an increase in the retention in GLC ("vicinal effect"), as shown by the elution order of dimethylphenols. This is similar to the retention behaviour of polyalkyl benzenes.

In GSC, large distances between the alkyl substituent and the phenolic hydroxyl group lead to increased retention.

TABLE II

FIRST- AND SECOND-ORDER RETENTION INDEX INCREMENTS FOR METHYL GROUPS, DEDUCED FROM THE RETENTION DATA OF METHYLPHENOLS AND DIMETHYLBENZENES AT 150°C

Increment	∂I_i^{PS}	$\partial I I_i^{OV}$	$\partial \Delta I_i$
$\partial I_{o\text{-methyl}}$	78	53	−25
$\partial I_{m\text{-methyl}}$	98	91	− 7
$\partial I_{p\text{-methyl}}$	97	89	− 8
H^{II}_{vic}	23	34	10
$H^{II}_{2,6}$	−10	−25	−15

In order to calculate the retention indices of dialkyl- or polyalkylphenols from the increments corresponding to the individual molecular fragments, the following equations were used

$$I_{\text{calc.}} = I_P + \Sigma \partial I_i$$
$$\Delta I_{\text{calc.}} = \Delta I_P + \Sigma \partial \Delta I_i$$

where $I_{\text{calc.}}$ is the calculated retention index and ∂I_i is the retention index increment of an individual molecular fragment.

To describe the discussed "*ortho*" and "vicinal" effects, second order increments are introduced[17] (Table II)

$$\Sigma \partial I_i = \partial I_{o\text{-R}} + \partial I_{m\text{-R}} + \partial I_{p\text{-R}} + H^{II}_{\text{vic}} + H^{II}_{2,6}$$

where o-R = an alkyl group in *ortho*-position, m-R = an alkyl group in *meta*-position, p-R = an alkyl group in *para*-position and H^{II} = second order increments of vicinal alkyl groups, H^{II}_{vic}, and of alkyl groups neighbouring the phenolic hydroxyl group, $H^{II}_{2,6}$.

As shown in Table III, the calculated values are in good agreement with the experimental data. The retention indices of other dialkylphenols have been calculated in the same manner. In the case of alkyl groups with more than three carbon atoms, the agreement was not satisfactory.

TABLE III

MEASURED AND CALCULATED VALUES FOR I^{PS}, I^{OV} AND ΔI OF DIMETHYLPHENOLS AT 150°C.

Phenol derivative	*Number of increments*					I^{PS}		I^{OV}		ΔI	
	o	*m*	*p*	*vic*	*2,6*	*Calc.*	*Exptl.*	*Calc.*	*Exptl.*	*Calc.*	*Exptl.*
2,6-Dimethyl-	2	–	–		1	1098	1096	1302	1299	204	203
2,4-Dimethyl-	1	–	1			1127	1128	1363	1359	236	231
2,5-Dimethyl-	1	1	–			1128	1130	1365	1360	237	230
3,5-Dimethyl-	–	2	–			1148	1146	1403	1399	255	253
2,3-Dimethyl-	1	1	–	1		1151	1159	1399	1401	247	242
3,4-Dimethyl-	–	1	1	1		1170	1172	1435	1432	264	260

CONCLUSIONS

The retention data of alkylphenols, obtained in GLC on PS-255 and on OV-1701-Vi, and in GSC on GTCB, can be explained only by considering both the electronic and steric effects of the alkyl groups and recognizing that both depend on the position and size of the alkyl groups.

The measured retention index data and the index increments are characteristic for the alkylphenol isomers and complement the structural information obtained by GC–MS analysis.

GSC on GTCB is advantageous for distinguishing between *meta*- and *para*-isomers, which are difficult to separate by GLC.

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