

CHROM. 14,474

PARTIAL EXPLANATION OF THE ANOMALY IN THE RELATIONSHIP BETWEEN THE LOGARITHM OF RETENTION AND THE CARBON NUMBER OF MONOHYDRIC PHENOLS

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(First received April 14th, 1981; revised manuscript received October 24th, 1981)

SUMMARY

An attempt was made to elucidate the anomaly in the $R_{t(\text{rel})} = f(C_n)$ function. It was found, that this anomaly results from complex and simultaneous actions of several factors. Hydrogen bond formation between the free phenolic hydroxyl group and the TXP polar stationary phase or between the functional groups themselves is certainly not the most important influencing factor. The conditions for using the $R_{t(\text{rel})} = f(C_n)$ function in identification of *n*-alkyl-substituted monohydric phenols were determined.

INTRODUCTION

In our previous papers^{1,2} retention data were published for a series of monohydric phenols. These data were obtained on a polar stationary phase of trixylenylphosphate (TXP)-phosphoric acid (95:5). Evaluating the interdependence of $\log R_{t(\text{rel})}$ (R_t = retention time) and the number of C atoms (C_n) in the molecule of monohydric phenol examined we proposed an anomalous course for this function.

TABLE I

RELATIVE RETENTION OF *n*-ALKYLPHENOLS ON APIEZON K

Phenol = 1; column temperature, 130°C (Fig. 3).

Substituent	Position of substituent			Number of substituents in molecule
	ortho	meta	para	
Methyl	1.25	1.69	1.73	7
Ethyl	1.9	2.72	2.83	8
<i>n</i> -Propyl	2.97	4.46	4.55	9
<i>n</i> -Butyl	5.17	7.79	8.08	10
<i>n</i> -Pentyl	9.28	—	14.91	11
<i>n</i> -Hexyl	15.63	—	25.46	12

TABLE II
COLUMN PARAMETERS AND CONDITIONS OF GC SEPARATION

	<i>Stationary phase</i>	
	<i>TXP-phosphoric acid (95:5)</i>	<i>Apiezon K</i>
Type of column	Open metal capillary	Open metal capillary
Length (m)	50	50
Inner diameter (mm)	0.25	0.25
Column temperature (°C)	125, 130	125, 130
Carrier gas	nitrogen	nitrogen
Nitrogen inlet pressure (kPa)	160	160
Split ratio	1:100	1:100
Evaporator temperature (°C)	250	250
Injected volume (sample size) (μ l)	0.5	0.5

The anomaly lies in an abrupt change in the slope of the plot at the point corresponding to *n*-propylphenol.

Owing to the impossibility of explaining this anomalous behaviour of C_9 isomers on the basis of literature data, we have now measured the retention data of some higher members of the homologous series of *n*-alkyl substituted monohydric phenols or similar substances on Apiezon K stationary phase (Table I).

Table II shows the column parameters and GC conditions for the compounds studied. The stationary phase (Apiezon K) was, unlike the TXP phase, non-polar.

In order to elucidate the possible influence of hydrogen bonds we carried out analogous measurements on the methyl ethers of 2- and 4-substituted *n*-alkylphenols, C_7 - C_{12} , prepared by the procedure of Sandermann and Weismann³ (Table III). The experiments were completed by determining the $R_{t(\text{rel})} = f(C_n)$ function of *n*-alkylbenzenes having a carbon skeleton identical with that of the monohydric phenols. The

TABLE III
RELATIVE RETENTION OF METHYL ETHERS OF *n*-ALKYLPHENOLS DETERMINED AT 125°C

<i>Alkyl phenyl ether of</i>	<i>Position of alkyl group</i>				<i>Number of C atoms in molecule</i>
	<i>ortho</i>		<i>para</i>		
	<i>Apiezon K*</i>	<i>TXP**</i>	<i>Apiezon K*</i>	<i>TXP**</i>	
Methylphenol	1.58	1.61	1.85	1.87	7
Ethylphenol	2.33	2.45	3.16	3.23	8
<i>n</i> -Propylphenol	3.63	3.85	5.31	5.31	9
<i>n</i> -Butylphenol	6.36	6.89	9.60	10.16	10
<i>n</i> -Pentylphenol	11.05	12.08	17.07	18.29	11
<i>n</i> -Hexylphenol	19.25	21.65	30.40	33.26	12

* Fig. 4.

** Fig. 5.

TABLE IV
RELATIVE RETENTION OF *n*-ALKYLBENZENES

Column temperature, 130°C (Fig. 6).

Compound	Stationary phase		Number of C-atoms in molecule
	Apiezon K	TXP	
Benzene	1.00	1.00	6
Methyl benzene	2.35	1.50	7
Ethyl benzene	4.35	2.12	8
<i>n</i> -Propyl benzene	7.65	3.09	9
<i>n</i> -Butyl benzene	14.58	5.15	10
<i>n</i> -Hexyl benzene	48.88	15.20	12
<i>n</i> -Nonyl benzene	296.88	84.47	15
<i>n</i> -Decyl benzene	—	147.20	16

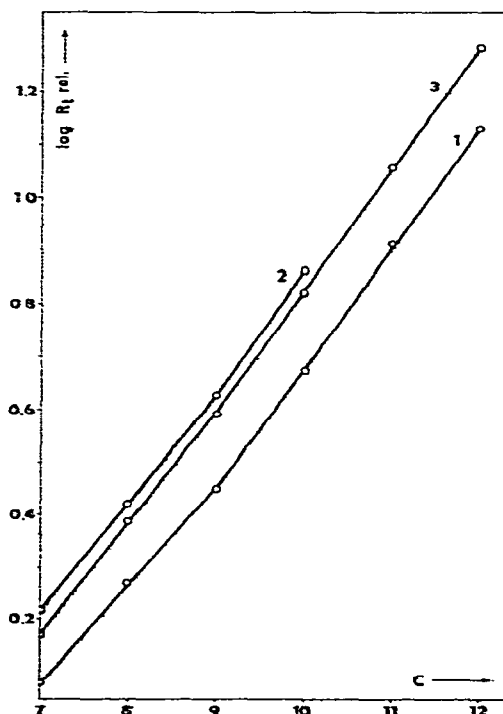
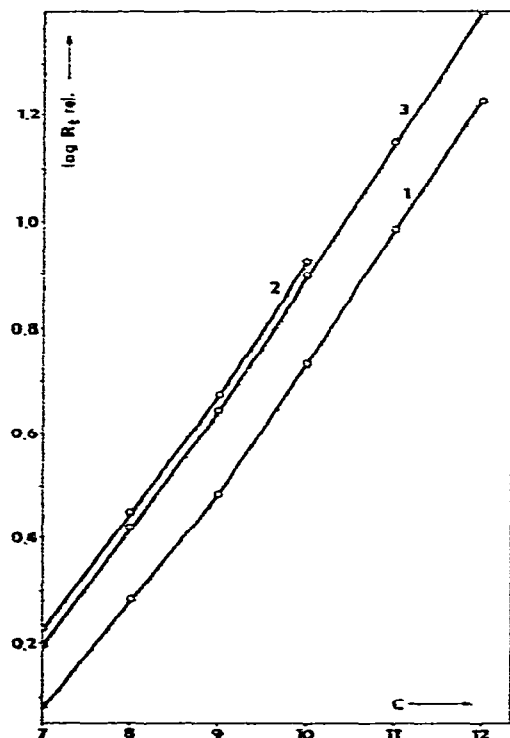


Fig. 1. Relationship between the logarithm of retention time and the carbon number for monohydric *n*-alkylphenols on a open capillary column coated with TXP-phosphoric acid (95:5) as stationary phase. Column temperature, 125°C. Lines: 1, 2-*n*-alkylphenols; 2, 3-*n*-alkylphenols; 3, 4-*n*-alkylphenols.

Fig. 2. Relationship between the logarithm of retention time and the carbon number for monohydric *n*-alkylphenols on a open capillary column coated with TXP-phosphoric acid (95:5) as stationary phase. Column temperature, 140°C. Lines: 1, 2-*n*-alkylphenols; 2, 3-*n*-alkylphenols; 3, 4-*n*-alkylphenols.

results are summarized in Table IV. To show the temperature independence of the data we repeated some measurements, which had previously been published¹, at a column temperature of 125°C. To achieve constant elution conditions an open-capillary column was used for all measurements.

RESULTS AND DISCUSSION

A critical interpretation of the results summarized in Tables I, III and IV enables us to make the following conclusions.

(1) The plot of the $\log R_{t(\text{rel})} = f(C_n)$ function for the homologous *n*-alkylmonosubstituted monohydric phenols has an anomalous course characterized by a sudden change in slope for all phenols substituted with alkyl substituent longer than *n*-propyl.

(2) This effect is temperature independent over the temperature range examined (125–140°C; Figs. 1 and 2).

(3) For the polar stationary phase the position of the change in slope rises as the *n*-alkyl group is moved nearer to the phenolic hydroxyl group. Very little change in the slope was observed for the 4-*n*-alkyl-substituted phenol series, while the change for the 3-*n*-alkyl-substituted series was more important, with that for the 2-*n*-alkyl-substituted phenols being the most significant.

(4) For the non-polar stationary phase (Apiezon K) there is also a sudden change of course in the plot of the $R_{t(\text{rel})} = f(C_n)$ function. Large differences in elution of 2-*n*- and 4-*n*-alkyl-substituted phenols up to C₉ are seen, but from this point the slopes of the plots for both series are identical (Fig. 3).

(5) Comparison of the plots of the $R_{t(\text{rel})} = f(C_n)$ functions for the non-polar and the polar stationary phases (TXP) showed an unambiguous relationship; in all cases the changes in slopes were more pronounced for the 2-*n*- and 4-*n*-alkyl series when a non-polar stationary phase was used. However for the 3-*n*-alkyl series, the changes were approximately the same on both the polar and non-polar stationary phases.

(6) Comparison of the plots of the $\log R_{t(\text{rel})} = f(C_n)$ functions for the polar stationary phase (TXP) with 2-*n*-alkylphenols and with their methyl ethers showed that etherification of the phenolic hydroxyl group leads to an increase in the differences in slope. Etherification of 4-*n*-alkylphenols caused only a small change in the shape of the graph; however there was also in this case a noticeable increase in the difference slope (Fig. 4).

(7) For the 4-*n*-alkylphenols series, using the non-polar stationary phase, the reverse influence of etherification to that observed for the TXP polar stationary phase is seen. The methyl ethers of 4-*n*-alkylphenols show a smaller change in the slope of the $R_{t(\text{rel})} = f(C_n)$ plot than the original 4-*n*-alkylphenol with a free phenolic function. The 2-*n*-alkylphenols do not change their behaviour and the difference in slope on Apiezon K remains approximately the same as that of the original 2-*n*-alkylphenols (Fig. 5).

(8) On the non-polar stationary phase the course of the $R_{t(\text{rel})} = f(C_n)$ function for the alkylbenzene series was linear with no change in slope. On the other hand a "break" in the linear plot was observed for the TXP polar stationary phase (Fig. 6).

The occurrence of "breaks" in the $R_{t(\text{rel})} = f(C_n)$ plot is in accordance with the

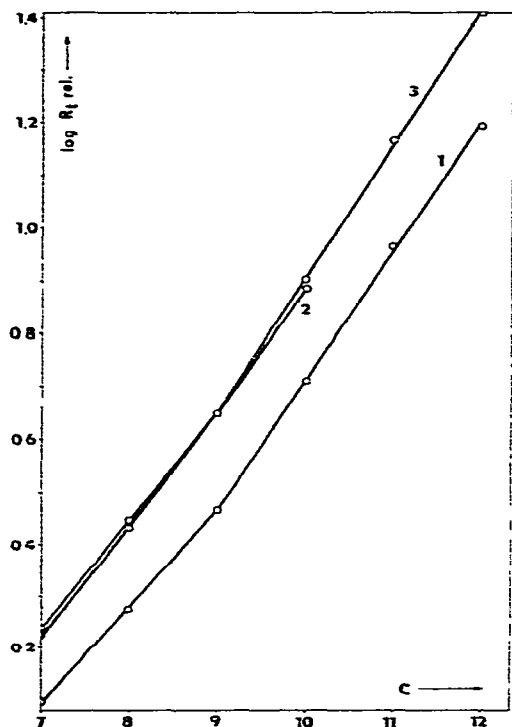


Fig. 3. Relationship between the logarithm of retention time and the carbon number for monohydric *n*-alkylphenols on a open capillary column coated with Apiezon K as stationary phase. Column temperature, 130°C. Lines: 1, 2-*n*-alkylphenols; 2, 3-*n*-alkylphenols; 3, 4-*n*-alkylphenols.

experimental results obtained on polar and non-polar stationary phases, motivated in these two different cases generally by two non-identical sets of influencing factors. This demonstrates for example the change of slope on the plot of $\log R_{t(\text{rel})} = f(C_n)$ determined by elution measurements of *n*-alkylbenzenes on the TXP polar stationary phase. On the basis of this plot of $R_{t(\text{rel})} = f(C_n)$ we presume a linkage between the conjugated double-bond system of the benzene aromatic ring and the polar stationary phase with the π -electrons of the aromatic ring playing a predominant role, strongly influenced by the degree of polarity of the stationary phase.

Because of the large amount of data necessary for the quantification and precise description of the bonds formed, it is so far impossible to describe and categorize the "complexes" formed with respect to the types defined in the literature.

In summary, these facts indicate that the anomaly in the gas-chromatographic behaviour is not caused by only one factor but by the complex and simultaneous action of several; the resulting effect can be comprehended only as a complex and mutually penetrating combination of them all.

However, in our work we can with certainty exclude hydrogen-bond formation between the free phenolic hydroxyl group and the stationary phase, or between the functional groups themselves, as being the most important factor causing the anomalous appearance of the $R_{t(\text{rel})} = f(C_n)$ graph. The "breaks" on the $R_{t(\text{rel})} = f(C_n)$ plot were found both for the *n*-alkylphenols and for the series of their methyl ethers, and,

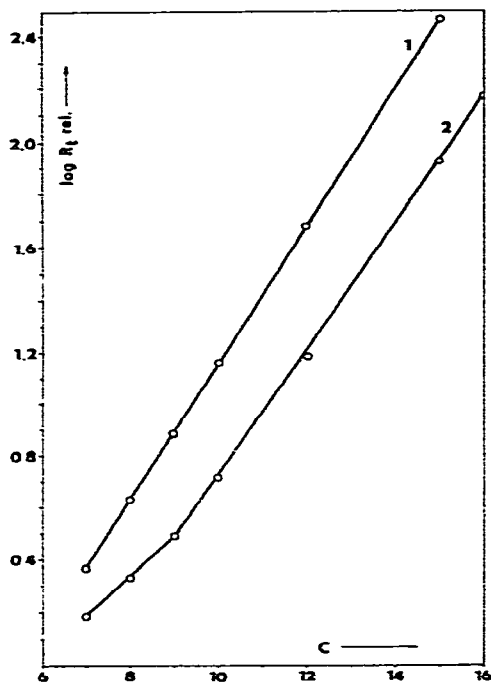
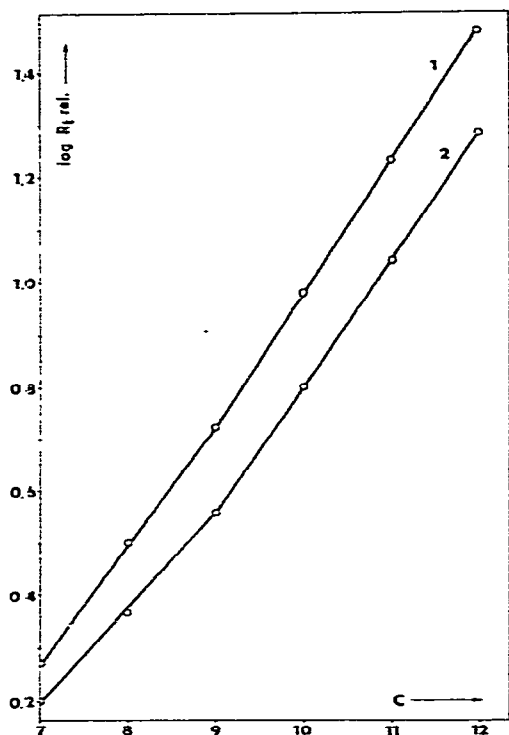


Fig. 4. Relationship between the logarithm of retention time and the carbon number for *n*-alkylphenyl methyl ethers (anisoles) on an open capillary column coated with TXP-phosphoric acid (95:5) as stationary phase. Column temperature, 125°C. Lines: 1, 2-*n*-alkylphenyl methyl ethers; 2, 4-*n*-alkylphenyl methyl ethers.

Fig. 5. Relationship between the logarithm of retention time and the carbon number for *n*-alkylphenyl methyl ethers (anisoles) on a open capillary column coated with Apiezon K as stationary phase. Column temperature, 125°C. Lines: 1, 2-*n*-alkylphenyl methyl ethers; 2, 4-*n*-alkylphenyl methyl ethers.

using the TXP polar stationary phase, also for the corresponding *n*-alkylbenzenes.

On the basis of the measurements it is possible to interpret the data as follows: the necessary condition for the existence of an anomaly in the $R_{t(\text{rel})} = f(C_n)$ graph for the non-polar stationary phase ("breaks") is the presence of a $C_{\text{ar}}-\text{O}$ bond in the molecules of the set of compounds studied.

With the polar stationary phase we find a somewhat different situation with regard to the presence of a $C_{\text{ar}}-\text{O}$ bond, because the anomaly in the $R_{t(\text{rel})} = f(C_n)$ plot also occurred for elution of *n*-alkylbenzenes. The inductive effect of the $C_{\text{ar}}-\text{O}$ bond on the aromatic nucleus of phenol and the ability to form hydrogen bonds increases here in importance especially with respect to the total number of influencing variables.

For the *n*-alkyl substituents $< C_3$ the difference in elution characteristics between two subsequent members of a homologous series, *i.e.* when increasing the molecule by a CH_2 group, is equal to the resultant of the altered induction forces between the aromatic nucleus and the alkyl substituent.

For the *n*-alkyl groups $> C_3$ the influence of this substituent on the retention

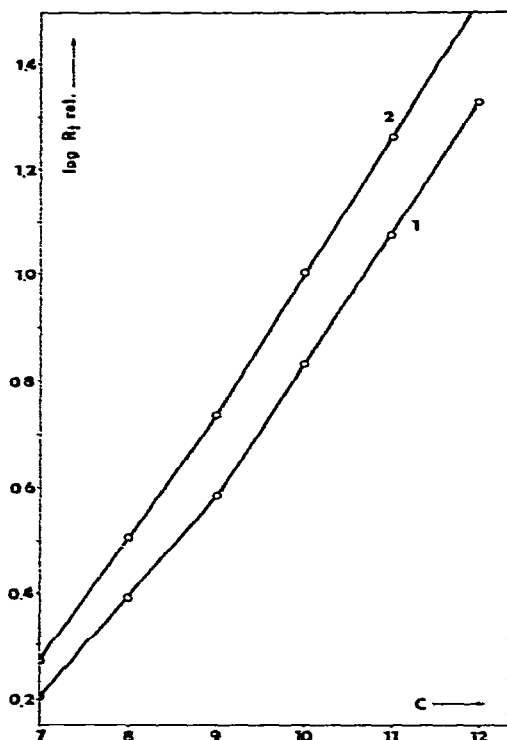


Fig. 6. Relationship between the logarithm of retention time and the carbon number for *n*-alkylbenzenes on a open capillary column coated with Apiezon K (line 1) or TXP-phosphoric acid (95:5) (line 2) as stationary phase. Column temperature, 130°C.

time (or the increase of this characteristic) relative to the CH₂ increment is substantially greater than in the case of a *n*-alkyl substituent < C₃. Here increasing the *n*-alkyl substituent by one CH₂ group does not significantly influence the π -electrons of the aromatic ring; the most important factor here will be solely the subsequent enlargement of the aromatic part of the molecule in question. When a hydroxyl group is introduced into a molecule of an *n*-alkylbenzene, the oxygen atom produces by its positive inductive effect a change in the distribution of electrons in the aromatic nucleus, causing a reduction in the bond-length between the π -electrons of the aromatic nucleus and the polar stationary phase. Nevertheless, these bonds play a part in the gas chromatography of *n*-alkylphenols.

Etherification of the phenolic hydroxyl group in the *n*-alkylphenols leads to a decrease in its inductive power enabling the aromatic nucleus to be better able to form, as described previously, a stronger bond with the polar stationary phase. However, the strength of this linkage is also proportional to the position of the phenolic hydroxyl group (or the methoxy group) in respect to the *n*-alkyl group in the original alkylbenzene molecule.

This interpretation is supported also by the fact that a shift of the alkyl substituent within the neighbourhood of the hydroxyl group produces an enhancement of "break" in the $R_{t(\text{rel})} = f(C_n)$ plot. The smallest differences in slope are charac-

teristic of the 4-*n*-alkylphenol series, larger differences being observed for the 3-*n*-alkylphenols: the largest differences occur for the 2-*n*-alkylphenols. On the basis of these results we conclude that the steric hindrance of hydrogen-bond formation (between the phenolic hydroxyl group and the stationary phase) enhances the other factors affecting the elution characteristics and which arise from the nature of the π -bonding between the stationary phase and the aromatic portion of the molecule.

CONCLUSIONS

In the identification of unknown phenols by gas chromatography on the polar TXP-phosphoric acid (95:5) phase we consider it indispensable when applying the $R_{t(\text{rel})} = f(C_n)$ relationship to determine by a reliable method the nature of the alkyl substituents present, before the chromatogram is interpreted. In the C₇-C₉ region, where the necessary standards are usually available, we can use the $R_{t(\text{rel})} = f(C_n)$ relationship directly by extrapolation or by interpolation. In all other cases this method provides wrong results. This statement is valid also for the elution of monohydric *n*-alkylphenols on the non-polar stationary phase Apiezon K and for the separation of *n*-alkylphenol ethers. In the latter case we confirmed this result for both the stationary phases studied (Apiezon K and TXP-phosphoric acid).

It is possible to presume an identical gas-chromatographic behaviour also for other homologous series (*e.g.* for nitrophenols, halogenated phenols, aminophenols, esters, silyl ethers, etc.). The characteristics of the stationary phases used (the elution was performed on both polar and non-polar stationary phases) provide evidence for the general validity of our conclusions for all types of stationary phases. The conclusion what a degree of polarity of the stationary phase causes the "break" in the $R_{t(\text{rel})} = f(C_n)$ plot for *n*-alkylbenzenes is not borne out by our results.

REFERENCES

- 1 J. Macák, P. Buryan and J. Hrivňák, *J. Chromatogr.*, 89 (1974) 309.
- 2 P. Buryan, J. Macák and J. Hrivňák, *J. Chromatogr.*, 137 (1977) 425.
- 3 W. Sandermann and G. Weismann, *Z. Anal. Chem.*, 189 (1962) 137.