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THE STERIC FACTOR IN GAS-LIQUID CHROMATOGRAPHIC RETENTION

F. VERNON

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs. (Great Britain)

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SUMMARY

The relationship between retention and structure of isomeric disubstituted benzenes has been investigated using the nitrobenzoic ester isomers. Retention data for methyl nitrobenzoates and nitrotoluenes on five stationary phases, Apiezon L, dodecyl dibenzoate and the three dodecyl nitrobenzoate isomers, show that selective retention occurs when the methyl ester has the same geometry as the stationary phase. This "steric effect" is quite small for the esters examined and is non-existent for retention of nitrotoluenes on nitro ester phases.

INTRODUCTION

Many of the solute-solvent interactions which occur during gas-liquid chromatographic separation—orientation effects, dispersion forces and hydrogen bonding¹—have been studied. In recent years, much work on correlation of retention data with structural parameters has been carried out on isomeric solutes where the simple additivity principle of the retention index (*I*) breaks down. Kováts and Strickler² were among the first to carry out such work, with a structural investigation based on ΔI values in the plinole series. Jonas and co-workers³ determined the significance of *I* values in substituted tetrahydrofurans and tetrahydropyrans but used only non-polar phases, Apiezon L and silicone grease. Haken⁴ correlated retention and structural parameters for several series of carbonyl compounds and Ackman and Castell⁵ studied the effect of structure on retention of fatty acids on a polyester stationary phase. Germaine and Haken^{6,7} examined retention properties of homologous esters on SE-30 and found that branched-chain isomers had lower retention indices than esters derived from *n*-alcohols. Schomberg⁸ has shown that the methyl esters of nonanecarboxylic acids, chromatographed on polypropylene sebacate and Carbowax 400, had a maximum increment, ΔI , over a squalane stationary phase when the carboxylic group was in the 1-position, the increment decreasing as the group approached the middle of the hydrocarbon chain.

The influence of molecular shape on ΔI for isomeric alkanes on a non-polar stationary phase was examined by Altenburg⁹, whilst Petsev and Dimitrov¹⁰, studying aliphatic hydrocarbons on phthalate ester stationary phases found a relationship between the structure of the stationary phase and the activity coefficients of the hydro-

carbons examined on benzenedicarboxylic esters. Cohesion forces were strongest when the ester alcohol chain was linear, lowest values were obtained when an aromatic ring structure was incorporated. The authors concluded that the steric position of the π orbitals diminishes the possibility of contact between solute and solvent molecules. Castello and D'Amato¹¹ have studied the alkyl iodides on tricresyl phosphate confirming Schomberg's work. Weiner and Howerly¹² have demonstrated the success of factor analysis for the prediction of retention indices based on molar polarization and dipole moment squared. Accurate predictions were obtained for the retention index of toluene on such widely different phases as silicone oil, polypropylene sebacate and Carbowax 20M. Bierl and co-workers¹³ have demonstrated the effect of functional group position in aliphatic isomeric alcohols, esters, ketones and ethers on four stationary phases and have shown that if an oxygen-containing group is located at positions 1, 2 or 3, its position could be determined from retention increment data.

Positional effects on retention have been studied for disubstituted and polysubstituted benzenes, Bark and Clarke¹⁴ have examined alkyl phenols and Mitchell and Vernon¹⁵ the nitrophenols and nitrocresols, explaining ΔI values for addition of a methylene group in terms of steric and electronic effects, hydrogen bonding and hyperconjugation. In addition to changing dipoles and generally altering the electron distribution when introducing a second substituent into a monosubstituted benzene, one can postulate a "steric factor" in retention due solely to the relative positions of the two groups on the benzene ring. It should therefore be possible to separate a particular isomer by preferential retention on a selected stationary phase provided that this steric effect is of sufficient magnitude. A simple model of the effect is provided by the theory of Glasstone *et al.*¹⁶ on viscous flow in simple liquids. The solute molecule is surrounded by other (solvent) molecules which have the effect of holding it in a cage. If the shape of the solvent cage resembles that of a particular isomer in a mixture, that isomer can occupy more solvent "holes" hence will be preferentially retained. To test this theory adequately, the stationary phase should be structurally similar to one of the three disubstituted benzene isomers. As previous work involved the separation and analysis of methyl nitrobenzoates¹⁷, it was decided that retention data for the three methyl nitrobenzoate isomers, together with methyl benzoate and nitrobenzene, should be obtained on three columns containing *o*-, *m*- and *p*-dodecyl nitrobenzoate, respectively, as stationary phases. At the high column temperatures required squalane could not be used, therefore Apiezon L was selected as the standard non-polar stationary phase. Unfortunately, dodecyl benzoate could not be used for comparison purposes so retention indices were obtained on a column containing the dibenzoic ester of 1,12-dodecanediol.

EXPERIMENTAL

Stationary phase and sample preparation

o-Nitrobenzoic acid was refluxed with thionyl chloride to produce the acid chloride. Half of the product was then heated with dodecanol at 50° overnight, the product was dissolved in chloroform, washed with sodium carbonate to remove unchanged acid chloride and free acid. After drying, the chloroform was removed by distillation, the product was then heated at 50° for 4 h under vacuum to remove volatiles. The remaining acid chloride was reacted with anhydrous methanol, the

product was dissolved in chloroform, washed as above, the solvent removed by distillation and the methyl ester purified by vacuum distillation. The *meta* and *para* isomers were prepared by the same procedure.

Columns

1 m × 6 mm O.D. copper tubing was packed with 10% w/w stationary phase on silylated Celite. The methyl nitrobenzoates were chromatographed with the two appropriate *n*-paraffins as 10% solutions in ether (sample size 5 μ l). Chromatographic data were obtained using a Pye 104 Series gas chromatograph with flame ionization detector (Pye Unicam, Cambridge, Great Britain). Retention times were measured directly by stopwatch, the dead volume being measured from *n*-paraffin peaks and checked by injections of coal-gas. All retention indices were obtained at a column temperature of 150°.

RESULTS AND DISCUSSION

The retention indices of methyl nitrobenzoates and nitrotoluenes, on the five stationary phases used, are given in Table I. The nitrotoluenes were included to determine whether a steric effect would be observed for any isomeric substituted nitrobenzenes or if a nitrobenzoic stationary phase would be selective only for nitrobenzoic esters. Benzene, toluene, nitrobenzene and methyl benzoate were included in order to calculate a theoretical retention index for nitrotoluene and methyl nitrobenzoate without taking isomerism into consideration.

It is apparent from Table I that any steric factor must play a minor role in retention, as the emergence of methyl nitrobenzoates on dodecyl nitrobenzoate stationary phases is always *ortho*, *para*, *meta*. The order of emergence of nitrotoluenes is *ortho*, *meta*, *para*. Table II gives the retention increments for the solutes,

TABLE I
RETENTION INDICES ON APIEZON L, DODECYL DIBENZOATE AND THE THREE ISOMERIC DODECYL NITROBENZOATE STATIONARY PHASES

Solute	Retention index (I)				
	Apiezon L	Dodecyl dibenzoate	Dodecyl <i>o</i> -nitro benzoate	Dodecyl <i>m</i> -nitro benzoate	Dodecyl <i>p</i> -nitro benzoate
Benzene	697	780	762	759	760
Toluene	801	887	870	871	869
Nitrobenzene	1103	1336	1299	1299	1282
Methyl benzoate	1093	1285	1255	1257	1253
Methyl <i>o</i> -nitrobenzoate	1354	1726	1694	1680	1659
Methyl <i>m</i> -nitrobenzoate	1443	1778	1725	1740	1712
Methyl <i>p</i> -nitrobenzoate	1436	1758	1699	1706	1694
<i>o</i> -Nitrotoluene	1166	1400	1365	1366	1351
<i>m</i> -Nitrotoluene	1213	1455	1417	1423	1404
<i>p</i> -Nitrotoluene	1228	1477	1442	1445	1425
Nitrotoluene (theoretical)	1207	1443	1407	1411	1391
Methyl nitrobenzoate (theoretical)	1499	1841	1792	1797	1775

TABLE II
RETENTION INCREMENTS OF SOLUTES ON DODECYL ESTERS OVER APIEZON L

Solute	Retention increment (ΔI)*			
	Dodecyl dibenzoate	Dodecyl <i>o</i> -nitrobenzoate	Dodecyl <i>m</i> -nitrobenzoate	Dodecyl <i>p</i> -nitrobenzoate
Benzene	83	65	62	63
Toluene	86	69	70	68
Nitrobenzene	233	196	196	179
Methyl benzoate	192	162	164	160
<i>o</i> -Nitro ester	372	340	326	305
<i>m</i> -Nitro ester	335	282	297	269
<i>p</i> -Nitro ester	322	263	270	258
<i>o</i> -Nitrotoluene	234	199	200	185
<i>m</i> -Nitrotoluene	242	204	210	191
<i>p</i> -Nitrotoluene	249	214	217	197

* Retention increment (ΔI) = $I_{\text{ester stationary phase}} - I_{\text{Apiezon L}}$.

being the difference between their retention indices on an ester stationary phase and on Apiezon L. Table II shows that, irrespective of stationary phase, the largest increment of the nitro ester solutes is provided by the *ortho* isomer and the smallest by the *para* isomer. However, on examining the behaviour of a particular methyl nitrobenzoate on the three nitro ester stationary phases, a small but significant steric effect is found. Thus the highest increment for the *ortho* ester solute is on the *ortho* stationary phase whilst that for the *meta* ester is on the *meta* phase. The *para* isomer does not seem to conform, however on the *ortho* stationary phase $\Delta I_m - \Delta I_p$ is 21, whilst on the *para* stationary phase the difference has fallen to only 12. Similarly on the *meta* stationary phase $\Delta I_o - \Delta I_p$ is 13 and on the *para* stationary phase it is only 5. The predominant factor in the retention increment would therefore appear to be dipole-dipole interaction and, as *p*-nitrocarbonyl compounds have the smallest dipole moments of the three isomers, retention increments of solutes on the *para* stationary phase should have lower values than on the two other isomeric phases. Furthermore, on dipole-dipole considerations, the increment shown by the *para* solute on the *para* stationary phase should have the lowest value of all. Both of the statements are seen to be correct on examining the values in Table II.

Comparison of solute behaviour on a nitrobenzoate stationary phase with the results on a dodecyl dibenzoate stationary phase also demonstrates the steric effect. On the dibenzoate, the incremental difference for *ortho*-*meta* methyl esters is 37 and for *meta*-*para* it is 13. On the *o*-nitro stationary phase, however, ΔI for *ortho*-*meta* has risen to 58 whilst *meta*-*para* has risen to 19. On the *p*-nitro stationary phase ΔI for *ortho*-*para* has the value of 36, "normal" when compared with dodecyl dibenzoate, whilst the *meta*-*para* increment has a value of 11 which, whilst being in agreement with the dodecyl dibenzoate result, is a significant decrease from the value obtained on the *o*-nitro stationary phase. A similar comparison of ΔI for methyl *o*-nitrobenzoate and methyl *p*-nitrobenzoate shows a difference on the dodecyl

dibenzoate stationary phase of 50, increasing to 77 when selective *ortho* retention is involved, having a value of 56 on the "neutral" *meta* phase with the lowest difference of 47 being given on the *para* phase where selective retention is again involved, this time for the *para* isomer.

Table III compares the differences in actual retention and the values calculated from the additivity principle. All nitro ester solutes show a lower retention than the theoretical value and this must be accounted for by solute-solute interactions reducing the solute-solvent interaction. In the nitrotoluene data, the *ortho* isomer is seen to have a lower than theoretical retention explainable in terms of intramolecular effect reducing the solute-solvent interaction. The *m*- and *p*-nitrotoluenes show an increased retention over the theoretical value indicating that solute-solvent interaction is favoured.

TABLE III

MEASURED RETENTION INCREMENTS OF SOLUTES OVER CALCULATED VALUES AND THE CONTRIBUTION OF THE STERIC FACTOR ($\delta\Delta I$) TO RETENTION

Solute	Retention increment $\Delta I = I_{\text{found}} - I_{\text{theory}}$			Selective increment ($\delta\Delta I$)
	Dodecyl <i>o</i> -nitro- benzoate	Dodecyl <i>m</i> -nitro- benzoate	Dodecyl <i>p</i> -nitro- benzoate	
<i>o</i> -Nitro ester	-98	-117	-116	+18.5 ± 0.5
<i>m</i> -Nitro ester	-67	-57	-63	+8 ± 2
<i>p</i> -Nitro ester	-93	-91	-81	+11 ± 1
<i>o</i> -Nitrotoluene	-42	-45	-40	+0.5 ± 2.5
<i>m</i> -Nitrotoluene	-10	+12	+13	-0.5 ± 1.5
<i>p</i> -Nitrotoluene	+35	+34	+34	-0.5 ± 0.5

The steric effect is shown in Table III, where each methyl isomer has its most positive increment on its corresponding isomer stationary phase. The selective increment due to this steric effect is expressed empirically as a selective increment, $\delta\Delta I$, being the increased retention of a solute on its own isomer stationary phase over the mean of its retention on the other two stationary phases. It is clear from an examination of $\delta\Delta I$ that a steric factor in retention is operating in the case of similar solutes and solvents, the nitrobenzoate esters. However, no steric relationship is found between the nitro ester stationary phases and isomeric nitrotoluenes.

The work described here has merely demonstrated the presence of a hitherto unmeasured effect in gas-liquid chromatographic retention. The explanation may lie in the steric configurations of solutes and stationary phases or possibly the phenomena could be explained purely in terms of dipole-dipole interaction. Obviously a more rigorous treatment is required on several systems, probably a most informative system for study would be one in which molecules with much larger dipoles are involved. The methoxy- or dimethylaminobenzoate isomers for instance should demonstrate this effect to a larger extent than the deactivating nitro-substituted esters on which this work has been carried out.

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