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## GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

### XXX\*. UNEXPECTED PREDOMINANCY OF POLAR EFFECTS OVER STERIC EFFECTS IN CROWDED ALIPHATIC ESTERS: A GAS-LIQUID CHROMATOGRAPHIC APPRAISAL OF SPECIFIC INTERACTIONS

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#### SUMMARY

The chromatographic behaviour of sixteen hindered  $\alpha,\alpha$ -disubstituted or  $\alpha,\alpha,\alpha$ -trisubstituted aliphatic ethyl or methyl esters having four to nine atoms in the acyl groups is presented. Kováts index increments,  $\Delta I$ , on height stationary phases of increasing polarity and the contributions of the methyl groups,  $\Delta Me$ , obtained by progressive substitution are discussed. The polar and steric effects can be separated by use of infra-red spectroscopic measurements and an extended Taft scale ( $-E_s^*$ ) ranging over eight powers of ten for the considered acyl groups. Predominancy of polar effects over steric effects is demonstrated for the congested  $\alpha,\alpha,\alpha$ -trisubstituted esters having seven to nine carbon atoms in the acyl group.

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#### INTRODUCTION

The importance of the competition between the polar and steric effects on specific interactions of alkanes with the different metal-ion forms of ion exchangers in gas-solid chromatography (GSC) has been described<sup>2-4</sup>. In order to improve knowledge of the selectivity of supports in GSC or of stationary phases in gas-liquid chromatography (GLC), the separation of polar and steric effects is needed<sup>2-5</sup>.

By physical organic chemical studies, the steric effects of various substituent groups have been described in terms of the Taft steric parameters, which have been extended to form a scale covering seven powers of  $10^{6-8}$ . For alkyl groups it is evident that when the groups contain more than six carbon atoms the contribution of ad-

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\* For Part XXIX, see ref. 1.

ditional carbon atoms is reduced. While there is a levelling effect, the Taft steric parameter remains high.

It is apparent that both polar and steric effects are varying simultaneously, however, the separation or determination of the relative contributions remains unresolved largely due to the studies of polar effects have been relative rather than absolute. However, some progress in the field of gas chromatography has been achieved and may be applied to this problem. Developments in data processing with the DARC topological analysis<sup>9</sup> allow a better understanding of the competition between polar and steric effects on the specific interactions between the solute and the stationary phase<sup>5</sup> or the adsorbent<sup>2,4</sup> in chromatography.

The structural effects in highly congested alkylacyl groups have been reported in GLC of a new series of hindered esters<sup>10</sup>. Chain branching or lengthening by the addition of alkyl groups is known to result in different contributions depending on whether it occurs in the acyl group or the alkanol chain<sup>5,11</sup>, and the recent work with hindered esters has allowed the effect in the vicinity of the carbonyl group to be studied<sup>10</sup>. It was observed that:

(a) elution on non-polar columns follows a boiling point order in common with simpler esters;

(b) when the polarity of the stationary phase is greatly increased the difference in retention between the  $\alpha,\alpha,\alpha$ -trisubstituted and the  $\alpha,\alpha$ -disubstituted esters is increased by a factor of 2. With the highly congested esters, even when some screening of the interactive carbonyl is possible, the retention is not reduced, but is further increased. It has been suggested that the polarity of the carbonyl group is increased, causing stronger specific interactions<sup>10</sup>.

In the present work, the relative contributions of steric and polar effects are demonstrated using gas chromatographic (GC) and spectroscopic data for with four series of congested esters wherein significant steric contributions might be expected.

## EXPERIMENTAL

The chromatographic data used have been published previously<sup>10</sup>. Chromatography was carried out using 12 ft.  $\times$  0.25 in. O.D. columns packed with 10% stationary phase on Chromosorb W AW DMCS, each operated isothermally at 120°C. The values are shown here (Table I) as  $\Delta I$  Kováts index retention increments, where  $\Delta I$  represents the difference between the retention indices on a polar, *e.g.*, Silar 10C, and a non-polar, here SE-30, stationary phase, and is expressed in index units (i. u.).

To evaluate the polarity of the ester carbonyl group, the carbonyl stretching frequency of the parent acids has been used according to MacPhee and co-workers<sup>12-14</sup>.

Fig. 1 gives the structure and affiliation of the population of crowded aliphatic esters. These compounds can be generated, formally, starting from methyl formate, taken as the focus FO, by progressive methyl substitution of the R acyl group from R = H up to hindered group with R having nine carbon atoms, in the vicinity of the carbonyl group, *i.e.*, compounds 17-19.

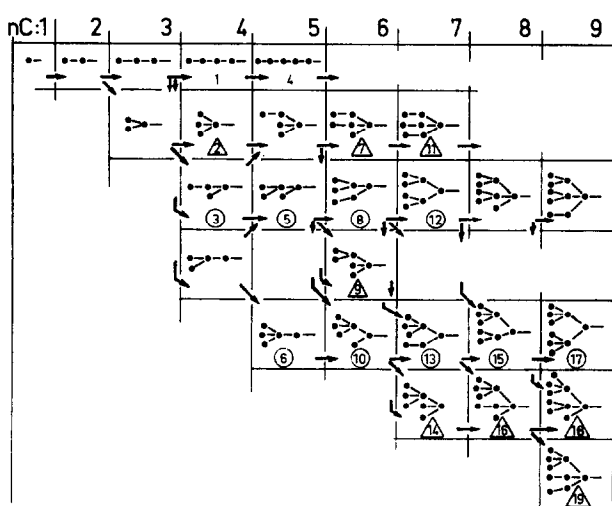


Fig. 1. Structure and affiliation of the population of crowded aliphatic esters  $RC(O)OR'$  obtained by progressive substitution of the R acyl group ( $R' = Et$  except for compound 14 for which  $R' = Me$ ). Chromatographic data for compounds inside boxes and with an identification number are presented in Table I.  $nC =$  Carbon atom number of the R acyl group.

## RESULTS AND DISCUSSION

Table I shows retention increments ( $\Delta I$  values) for the esters studied, which largely comprise two groups of  $\alpha, \alpha$ -disubstituted and  $\alpha, \alpha, \alpha$ -trisubstituted hindered esters having four to nine carbon atoms in the acyl groups. From the table the effect of the specific interaction  $\Delta I$  is evident; it represents 1/3 to 1/4 of the measured retention on the five more polar phases OV-105 to Silar 10C. The retention of the esters and  $\Delta I$  values increase with increasing stationary phase polarity due to the presence of an increasing amount of cyano or other polar groups, *i.e.*, PEG 400.

The relative effect of tri- and disubstitution of the acyl group at the carbon atom in the  $\alpha$  position relatively to the carbonyl group is apparent from Table I. For the same total carbon number ( $C_7$ – $C_9$ ) the  $\Delta I$  values of trisubstituted esters are greater than for the isomeric  $\alpha, \alpha$ -disubstituted esters on the more polar columns.










Fig. 2 shows the influence of the introduction of methyl groups in the affiliation series of the crowded aliphatic esters presented in Fig. 1. The index differences,  $\Delta Me$ , between two consecutive compounds in the affiliation series on the eight stationary phases of increasing polarity, from SE-30 to Silar 10C, are shown. For compounds with acyl groups having carbon atom numbers,  $n$ , equal to 4, 5 or 6 the  $\Delta Me$  values obtained on the eight stationary phases are relatively low and constant, irrespective of polarity, *i.e.*, 68–82 i.u. for  $\Delta Me$  (3  $\rightarrow$  5), 57–87 i.u. for  $\Delta Me$  (5  $\rightarrow$  8) or 79–99 i.u. for  $\Delta Me$  (6  $\rightarrow$  10). The first two ranges correspond to affiliation between  $\alpha, \alpha$ -disubstituted esters and the third one between a mono- and an  $\alpha, \alpha$ -disubstituted ester. The lowest range (44–66 i.u.) is observed for  $\Delta Me$  (5  $\rightarrow$  9), *i.e.*, for an affiliation between an  $\alpha, \alpha$ -disubstituted and an  $\alpha, \alpha, \alpha$ -trisubstituted ester where hindrance begins to be observed in the vicinity of the carbonyl group<sup>5</sup>.

For compounds with acyl groups where  $n$  is greater than 6, drastic changes are

TABLE I  
*AI* RETENTION INCREMENTS OF HINDERED ESTERS ON SEVEN STATIONARY PHASES OF INCREASING POLARITY

The esters are numbered as previously<sup>10</sup>; all are ethyl esters except 14 which is a methyl ester.

No. Ester	Acyl group	n	OV-7	OV-25	OV-105	PEG 400	Silar 7CP	Silar 9CP	Silar 10C
1 Ethyl pentanoate		4	—	138	—	—	—	—	—
2 Ethyl 2,2-dimethylpropanoate		4	38	—	—	—	—	—	—
3 Ethyl 2-methylbutanoate		4	48	125	317	318	351	392	429
4 Ethyl hexanoate		5	69	142	—	—	—	—	—
5 Ethyl 2,3-dimethylbutanoate		5	49	122	325	312	352	388	426
6 Ethyl 3,3-dimethylbutanoate		5	47	113	310	305	341	386	442
8 Ethyl 2-ethyl-3-methylbutanoate		6	47	118	308	298	334	400	437
9 Ethyl 2,2,3-trimethylbutanoate		6	43	113	307	291	330	386	426
10 Ethyl 2,3,3-trimethylbutanoate		6	46	116	311	297	336	398	439

11	Ethyl 2,2-diethylbutanoate		7	48	121	325	300	342	401	441
12	Ethyl 2-isopropyl-3-methylbutanoate		7	50	118	315	287	334	367	402
13	Ethyl 2-ethyl-3,3-dimethylbutanoate		7	37	109	—	—	—	356	392
14	Methyl 2,2,3,3-tetramethylbutanoate		7	49	130	343	333	371	420	465
15	Ethyl 2-isopropyl-3,3-dimethylbutanoate		8	83	179	287	270	311	349	407
16	Ethyl 2-ethyl-2,3,3-trimethylbutanoate		8	48	125	331	302	349	397	460
17	Ethyl 3,3-dimethyl-2-tert.-butylbutanoate		9	43	113	306	281	319	365	402
18	Ethyl 3,3-dimethyl-2-isopropyl-2-methylbutanoate		9	55	140	—	329	—	439	482
19	Ethyl 3,3-dimethyl-2,2-diethylbutanoate		9	49	129	349	316	356	411	450

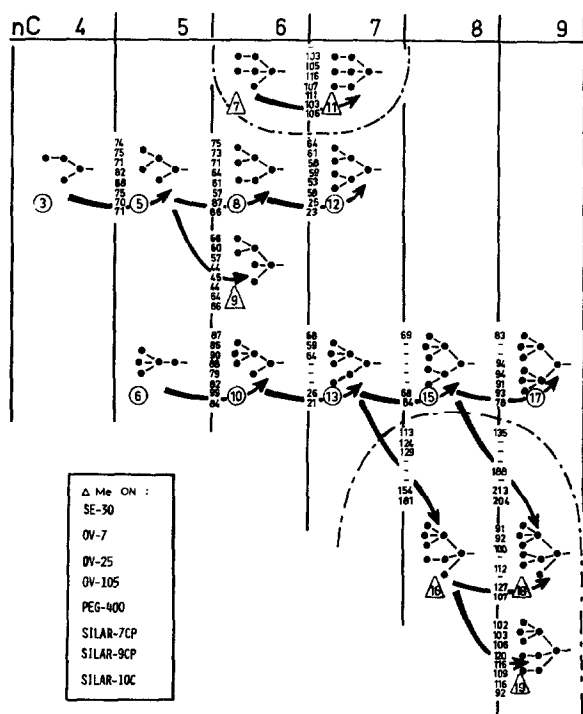


Fig. 2. Influence of the progressive introduction of methyl groups, in the affiliation series of crowded aliphatic esters, on the variation of retention indices,  $\Delta Me$ , on the eight stationary phases of increasing polarity, from SE 30 to Silar 10C.

observed, Fig. 2, and can be divided into two categories: affiliation between  $\alpha, \alpha$ -disubstituted esters and affiliation involving  $\alpha, \alpha, \alpha$ -trisubstituted esters. For affiliation between  $\alpha, \alpha$ -disubstituted esters the  $\Delta Me$  values remain lower than 100 index unit (i.u.). Where hindrance begins to be significant, *i.e.*, with two isopropyl groups,  $\Delta Me$

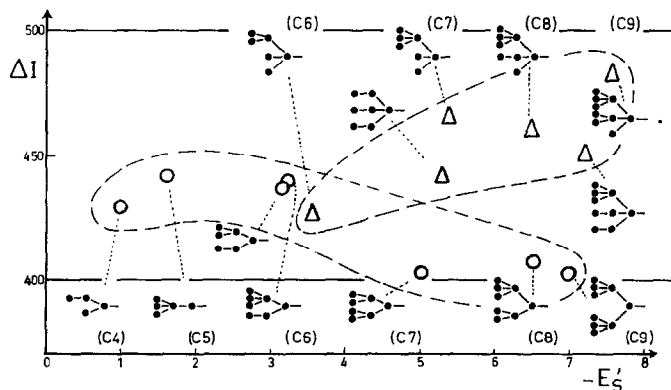


Fig. 3. Specific interaction,  $\Delta I$ , on Silar 10C versus the Taft steric parameter,  $-E_s$ . For the  $\alpha, \alpha, \alpha$ -trisubstituted esters ( $\Delta$ ) the specific interaction increases with the Taft steric parameter, while the opposite is observed for the  $\alpha, \alpha$ -disubstituted esters (O).

(8 → 12), the Me value is low ( $\approx 60$  i.u.) and decreases significantly with increasing stationary phase polarity ( $\Delta\text{Me} = 23$  i.u. on Silar 10C). The same effect occurs when progressing from a methyl to an ethyl group with an adjacent tertiary butyl group, affiliation 10 → 13. Then, when the polarity of the stationary phase increases, for  $n = 6 \rightarrow 7$ ,  $\Delta\text{Me}$  decreases by about a factor of 3. When branching commences at the second substituent (13 → 15) or increases (15 → 17), the  $\Delta\text{Me}$  value is a little higher and is relatively constant.

On the contrary, for affiliation involving  $\alpha,\alpha,\alpha$ -trisubstituted esters, with  $n \geq 7$  the contribution of a methyl group,  $\Delta\text{Me}$ , is mostly in excess of 100 i.u. Furthermore, when the polarity of the stationary phase increases, no decrease of the  $\Delta\text{Me}$  value is observed, and when the affiliation is between an  $\alpha,\alpha$ -disubstituted and an  $\alpha,\alpha,\alpha$ -trisubstituted ester,  $\Delta\text{Me}$  increases greatly to about 200 i.u. These observations complement our earlier report on the difference in retention behaviour between crowded  $\alpha,\alpha,\alpha$ -trisubstituted and  $\alpha,\alpha$ -disubstituted esters<sup>10</sup>.

### Influence of steric effects

The steric effect is demonstrated in Fig. 3 with data on Silar 10C. For disubstituted esters the specific interaction ( $\Delta I$ ) decreases as the Taft steric parameter,  $-E_s$ , increases greatly over a range of six powers of  $10^9$ . In comparison, the trisubstituted esters show an increase in  $\Delta I$  with increasing  $-E_s$ . With the same  $-E_s$  values, the variation of  $\Delta I$  is approximately 80 i.u. for the  $C_9$  groups.

With less crowded esters there is some protection of the carboxyl group with branching of the acyl group close to the carbonyl group. This protection becomes more evident with increasing polarity of the stationary phase and has been quantified by considering the behaviour of aliphatic esters on Silar 5CP using topological analyses<sup>5</sup>. For example, for propionate and isobutyrate esters the increased retention is only about 1.2 index units despite the presence of an additional methyl group<sup>5</sup>.

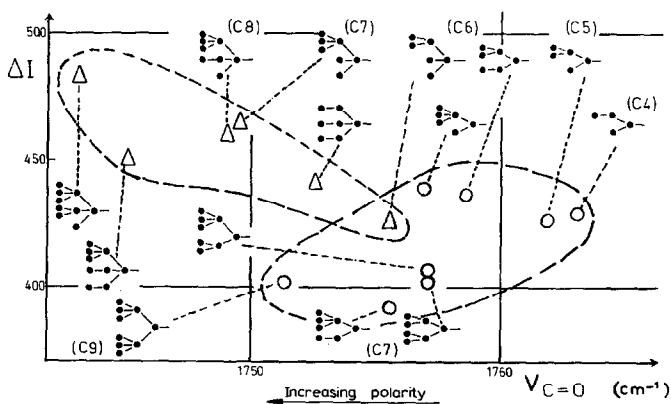


Fig. 4. Specific interactions,  $\Delta I$ , on Silar 10C versus the infra-red carbonyl stretching frequencies of the corresponding acids. When  $\nu_{C=O}$  ( $\text{cm}^{-1}$ ) decreases the polarity of the carbonyl group increases. The  $\alpha,\alpha,\alpha$ -trisubstituted esters ( $\Delta$ ) with seven or more carbon atoms in the acyl group are more polar than the  $\alpha,\alpha$ -disubstituted esters ( $\circ$ ) having the same carbon atom number.

### *Influence of polarity*

Fig. 4 shows the influence of polarity on the specific interaction as evidenced by the infra-red carbonyl stretching frequencies of the corresponding acids. A decrease in frequency corresponds to an increase in polarity, as demonstrated previously<sup>12,13</sup>. For the disubstituted esters, when the steric effects increase the polarity increases simultaneously but the steric effects are predominant; the specific interaction  $\Delta I$  decreases. For the trisubstituted esters, where the steric effect increases in by four powers of 10, we observe a large variation in the polarity which explains the strong increase in the specific interaction  $\Delta I$ . The most polar compound will be the *tert.*-butyl, isopropyl, methyl-trisubstituted acetate. We observe an increase of more than 50 index units over the range of trisubstituted esters, which demonstrates clearly that for the overcrowded compounds ( $C_7$ - $C_9$ ) there is a strong increase in the polar effects which become predominant over the noticeable steric effect.

### CONCLUSIONS

A series of hindered aliphatic esters with steric effects ranging over eight powers of ten, derived by progressive substitution of the acyl group, has been studied by gas chromatography. It allows a separation of the polar and steric effects using complementary data from IR measurements and the extended Taft scale.

Despite the potential shielding of the carbonyl group of the crowded esters, all observations suggested modification of the hybridization of the carbon atom  $\alpha$  to the carbonyl group for the more hindered trisubstituted esters, toward  $2p$  hybridization. Accordingly, this chromatographic method can be employed as a sensor of the polarity of the compounds and is more sensitive than measurement of  $pK_a$  values of the corresponding acids.

### ACKNOWLEDGEMENT

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