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## KOVÁTS RETENTION INDICES IN THE IDENTIFICATION OF ALKYL-BENZENE DEGRADATION PRODUCTS

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### SUMMARY

The Kováts retention indices of a large number of alkylbenzenes on different selective phases were determined. On the basis of incremental values,  $\delta I$ , on SE-30 as the liquid phase, the alkylbenzene degradation products were identified. The retention indices derived using homeomorphism factors for particular components were in very good agreement regardless of the parent compound and substituents used in deriving the retention data.

The incremental values for 38 alkyl and alkenyl substituents were determined, and the results obtained permitted the identification of more than 80 aromatic compounds evolved from alkylbenzene pyrolysis.

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### INTRODUCTION

Kováts retention indices<sup>1-3</sup> are used extensively in gas chromatographic identifications, especially when other identification methods are not applicable, usually due either to the lack of the pure substances needed or the unavailability of other suitable methods and techniques. Literature data on the alkylbenzene and alkenylbenzene retention indices, especially for higher homologues, are scarce.

Loewenguth and Tourres<sup>4</sup> carried out the hydrocarbon group analysis of complex hydrocarbon mixtures using Kováts indices for the identification of the components. Aliev *et al.*<sup>5</sup> developed a method for the separation and determination of C<sub>8</sub>-C<sub>12</sub> alkylbenzenes based on relative retention volumes. Schomburg used retention indices, including structural increments, for the identification of the components of an isomeric hydrocarbon mixture with mass spectrometric control of the results obtained<sup>6</sup>. Bonastre and Grenier<sup>7</sup> studied the activity coefficients of liquid phases by considering the retention data for alkylbenzenes. From the relationships obtained, they calculated the retention indices of 12 alkylbenzenes on 11 stationary phases. Kováts retention indices of lower alkylbenzenes on modified alumina as the stationary phase were determined by Vernon<sup>8</sup>. The validity of the relationships between the structure of C<sub>6</sub>-C<sub>10</sub> alkylaromatics and their retention data has been studied recently<sup>9-11</sup>, and an empirical relationship between the Kováts indices and a proposed substitution constant was determined. The validity of the correlation obtained was proved experimentally and used in the identification of some C<sub>11</sub> alkylaromatics. Recently, Takács and co-

workers<sup>12,13</sup> introduced an index system involving the use of so-called "bond increments" to enable Kováts retention indices to be predicted.

The homeomorphism factors or increments, the values of which are closely related to molecular structure<sup>6,14-16</sup>, are of help in the identification of components and also in the prediction of retention indices.

This work was carried out in order to identify the very complex mixture of alkylbenzene degradation products. As we lacked all the pure substances needed in order to determine retention indices experimentally, it was necessary, however, to calculate the retention indices on the basis of homeomorphism factors.

## EXPERIMENTAL

The pyrolysis of alkylbenzenes was carried out in a micro-flow reactor with a gold capillary tube<sup>17,18</sup>. The analysis and determinations of retention indices were performed on a Becker (Delft, The Netherlands) Model 1452 DPF gas chromatograph with a flame ionization detector.

The retention indices of alkylbenzenes were studied on four capillary columns, with helium as carrier gas, under the following operating conditions:

- (1) Column: glass, SE-30, 25.5 m × 0.50 mm I.D.; temperature 65°; splitting ratio 1:67.
- (2) Column: stainless steel, Citroflex A-4, 10.5 m × 0.25 mm I.D.; temperature 70° and 90°; splitting ratio 1:130.
- (3) Column: stainless steel, squalane, 50 m × 0.2 mm I.D.; temperature 100°; splitting ratio 1:100.
- (4) Column: stainless steel, Carbowax 6000, 10 m × 0.25 mm I.D.; temperature 90°; splitting ratio 1:150.

The column efficiencies expressed as the theoretical plate number ( $N$ ) and height equivalent to a theoretical plate (HETP) for particular columns were as follows: (1)  $N = 2.0 \cdot 10^4$ , HETP =  $12 \cdot 10^{-4}$ ; (2)  $N = 1.2 \cdot 10^4$ , HETP =  $8.7 \cdot 10^{-4}$ ; (3)  $N = 4.6 \cdot 10^4$ , HETP =  $1.1 \cdot 10^{-4}$ ; (4)  $N = 4.6 \cdot 10^3$ , HETP =  $21.6 \cdot 10^{-4}$ .

All the compounds investigated were API standard samples. Research-grade methane used for the determination of  $t_0$  was the product of Phillips Petroleum Co. Injections of samples were made with a Hamilton 1- $\mu$ l syringe.

The retention data obtained from the SE-30 capillary column were used for the identification of alkylbenzene degradation products.

## RESULTS

The Kováts retention indices of the alkylbenzenes examined on the columns described above are tabulated in Tables I and II. All the values are the averages of at least four measurements. The repeatability of the measurements is given as the relative standard deviation. Values found in the literature for retention indices on squalane and SE-30 columns are also included in Table I ( $I_{lit.}$ ). The operating temperatures at which these results were obtained are given in parentheses.

Table III shows the Kováts retention indices of aromatics other than alkylbenzenes, as alkylbenzene degradation products.

TABLE I

RETENTION INDICES OF ALKYL BENZENES ON SQUALANE (S) AND SILICONE RUBBER SE-30 (SE-30)

No. Compound	$I_{100}^S$	$\sigma_{ret.}$ ( $\pm$ %)	$I_{lit.}^S$	$I_{65}^{SE-30}$	$\sigma_{ret.}$ ( $\pm$ %)	$I_{lit.}^{SE-30}$
1 Benzene	650.4	0.33	648.9 (86°) <sup>20</sup> 650.6 (92°) <sup>24</sup>	654.8	0.21	656 (75°) <sup>21</sup>
2 Toluene	758.0	0.15	755.8 (86°) <sup>20</sup> 758.0 (92°) <sup>24</sup>	757.6	1.02	759 (75°) <sup>21</sup>
3 Ethylbenzene	847.7	0.09	843.5 (80°) <sup>4</sup> 846.4 (86°) <sup>20</sup>	849.1	1.59	855 (50°) <sup>22</sup>
4 <i>p</i> -Xylene	861.8	0.08	859.1 (80°) <sup>4</sup> 861 (92°) <sup>9</sup>	857.8	0.90	877 (100°) <sup>22</sup>
5 <i>m</i> -Xylene	863.2	0.09	856.5 (80°) <sup>4</sup> 863.0 (92°) <sup>9</sup>	857.8	0.90	879 (100°) <sup>22</sup>
6 <i>o</i> -Xylene	883.7	0.05	878.7 (80°) <sup>4</sup> 883 (92°) <sup>9</sup>	878.9	0.43	901 (100°) <sup>22</sup>
7 Isopropylbenzene	908.0	0.06	909 (120°) <sup>7</sup>	910.1	0.71	916 (28°) <sup>23</sup>
8 <i>n</i> -Propylbenzene	936.1	0.10	938 (100°) <sup>7</sup> 941.3 (100°) <sup>6</sup>	938.1	0.59	
9 1-Methyl-3-ethylbenzene	948.6	0.25	948 (92°) <sup>9</sup>	948.2	0.01	
10 1-Methyl-4-ethylbenzene	951.3	0.22	950 (92°) <sup>9</sup>	948.2	0.01	
11 1-Methyl-2-ethylbenzene	964.7	0.06	964 (92°) <sup>9</sup>	963.2	0.12	
12 1,3,5-Trimethylbenzene	967.6	0.04	968.0 (120°) <sup>7</sup>	952.1	0.20	994 (125°) <sup>21</sup>
13 <i>tert.</i> -Butylbenzene	973.3	0.05		975.4	0.11	976 (28°) <sup>23</sup>
14 1,2,4-Trimethylbenzene	988.2	0.00	990 (120°) <sup>7</sup>	974.9	0.18	
15 Isobutylbenzene	989.8	0.03	985 (120°) <sup>7</sup>	993.1	0.43	
16 <i>sec.</i> -Butylbenzene	989.8	0.03	995.2 (100°) <sup>6</sup>	993.1	0.43	
17 1-Methyl-3-isopropylbenzene	1002.4	0.04	1002 (92°) <sup>24</sup>	998.1	0.15	
18 1-Methyl-4-isopropylbenzene	1011.0	0.03	1005.0 (120°) <sup>7</sup> 1010 (92°) <sup>24</sup>	1003.2	0.23	
19 1,2,3-Trimethylbenzene	1011.9	0.02		1005.2	0.34	
20 1-Methyl-2-isopropylbenzene	1016.4	0.01	1015 (92°) <sup>9</sup>	1016.9	0.38	
21 1,3-Diethylbenzene	1028.9	0.12		1031.5	0.00	
22 1-Methyl-3- <i>n</i> -propylbenzene	1033.4	0.04	1033 (92°) <sup>9</sup> 1033 (92°) <sup>24</sup>	1031.6	0.25	
23 <i>n</i> -Butylbenzene	1035.8	0.39	1041 (100°) <sup>6</sup> 1033 (120°) <sup>7</sup>	1037.4	0.16	
24 1,4-Diethylbenzene	1039.1	0.30		1037.1	0.29	
25 1-Methyl-4- <i>n</i> -propylbenzene	1039.3	0.03	1039 (92°) <sup>24</sup>	1035.4	0.18	
26 1,2-Diethylbenzene	1039.1	0.30		1042.7	0.12	
27 1-Methyl-2- <i>n</i> -propylbenzene	1046.3	0.01	1045 (92°) <sup>24</sup>	1045.8	0.04	
28 1,3-Dimethyl-5-ethylbenzene	1048.2	0.17		1042.7	0.12	
29 1,4-Dimethyl-2-ethylbenzene	1060.0	0.15		1060.5	0.34	
30 1-Methyl-3- <i>tert.</i> -butylbenzene	1062.3	0.01		1067.5	0.05	
31 1,3-Dimethyl-4-ethylbenzene	1066.6	0.19		1060.5	0.34	
32 <i>tert.</i> -Pentylbenzene	1070.3	0.07		1070.5	0.09	
33 1,2-Dimethyl-4-ethylbenzene	1072.0	0.12		1066.0	0.00	
34 1,3-Dimethyl-2-ethylbenzene	1072.0	0.12		1070.4	0.04	
35 1-Methyl-4- <i>tert.</i> -butylbenzene	1075.6	0.04		1072.2	0.19	
36 <i>sec.</i> -Pentylbenzene	1078.1	0.09		1082.1	0.00	
37 1,2-Dimethyl-3-ethylbenzene	1088.1	0.06		1082.5	0.20	
38 1,2,4,5-Tetramethylbenzene				1094.9	0.12	
39 1,2,3,5-Tetramethylbenzene				1097.7	0.14	
40 1,3-Diisopropylbenzene				1135.2	0.64	
41 <i>n</i> -Pentylbenzene			1137.6 (100°) <sup>6</sup>	1135.2	0.64	
42 1,2,3,4-Tetramethylbenzene				1125.6	0.46	
43 1,4-Diisopropylbenzene				1152.0	0.54	
44 1,3-Dimethyl-5- <i>tert.</i> -butylbenzene				1152.0	0.54	
45 1,3,5-Triethylbenzene				1158.1	0.39	

TABLE II

RETENTION INDICES OF ALKYL BENZENES ON CITROFLEX A-4 (Cit. A-4) AND CARBOWAX 6000 (Carb. 6000)

No. Compound	$I_{70}^{Cit. A-4}$	$\sigma_{rel.}$ ( $\pm\%$ )	$I_{90}^{Cit. A-4}$	$\sigma_{rel.}$ ( $\pm\%$ )	$I_{90}^{Carb. 6000}$	$\sigma_{rel.}$ ( $\pm\%$ )
1 Benzene	779.9	0.25				
2 Toluene	881.1	0.11				
3 Ethylbenzene	971.2	0.30				
4 <i>p</i> -Xylene	978.5	0.10				
5 <i>m</i> -Xylene	981.4	0.40				
6 <i>o</i> -Xylene	1007.9	0.25				
7 Isopropylbenzene	1029.4	0.32				
8 <i>n</i> -Propylbenzene	1056.4	0.43				
9 1-Methyl-3-ethylbenzene	1068.8	0.19				
10 1-Methyl-4-ethylbenzene	1068.8	0.19				
11 1,3,5-Trimethylbenzene	1078.6	0.09				
12 1-Methyl-2-ethylbenzene	1089.8	0.09				
13 1,2,4-Trimethylbenzene	1095.3	0.26				
14 <i>tert.</i> -Butylbenzene	1095.7	0.01				
15 Isobutylbenzene	1105.3	0.51				
16 <i>sec.</i> -Butylbenzene	1108.4	0.53				
17 1-Methyl-3-isopropylbenzene	1119.0	0.46				
18 1-Methyl-4-isopropylbenzene	1123.7	0.02				
19 1,2,3-Trimethylbenzene	1134.6	0.26				
20 1-Methyl-2-isopropylbenzene	1140.4	0.14				
21 1,3-Diethylbenzene	1149.4	0.11				
22 1-Methyl-3- <i>n</i> -propylbenzene	1149.7	0.07				
23 1-Methyl-4- <i>n</i> -propylbenzene	1153.1	0.12				
24 <i>n</i> -Butylbenzene	1157.3	0.11				
25 1,4-Diethylbenzene	1158.0	0.00				
26 1,2-Diethylbenzene	1165.4	0.21				
27 1,3-Dimethyl-5-ethylbenzene	1165.4	0.21				
28 1-Methyl-2- <i>n</i> -propylbenzene	1168.2	0.11				
29 1,4-Dimethyl-2-ethylbenzene	1180.7	0.01				
30 1-Methyl-3- <i>tert.</i> -butylbenzene	1183.8	0.15				
31 1,3-Dimethyl-4-ethylbenzene	1186.2	0.03				
32 <i>tert.</i> -Pentylbenzene	1189.3	0.15				
33 1,2-Dimethyl-4-ethylbenzene	1191.7	0.02				
34 1-Methyl-4- <i>tert.</i> -butylbenzene	1193.5	0.17			1355.1	1.14
35 1,3-Dimethyl-2-ethylbenzene	1200.0	0.00				
36 <i>sec.</i> -Pentylbenzene	1200.0	0.00				
37 1,2-Dimethyl-3-ethylbenzene			1220.5	0.87	1430.8	0.16
38 1,2,4,5-Tetramethylbenzene			1232.1	0.84	1445.8	0.25
39 1,2,3,5-Tetramethylbenzene			1238.9	1.05	1455.8	0.33
40 1,3-Diisopropylbenzene			1242.7	0.68	1376.0	0.62
41 <i>n</i> -Pentylbenzene			1260.7	0.46	1433.3	0.07
42 1,2,3,4-Tetramethylbenzene			1270.9	0.39		
43 1,4-Diisopropylbenzene			1270.9	0.39	1417.6	0.10
44 1,3-Dimethyl-5- <i>tert.</i> -butylbenzene			1275.0	0.37	1430.8	0.16
45 1,3,5-Triethylbenzene			1314.8	1.03	1476.5	0.47
46 1,2,3,4,5-Pentamethylbenzene			1391.3	0.98		
47 1,3,5-Triisopropylbenzene					1495.2	0.12

TABLE III

RETENTION INDICES OF SOME AROMATIC COMPOUNDS ON SILICONE RUBBER SE-30

No.	Compound	$I_{65^\circ}^{SE-30}$	$I_{117^\circ}^{SE-30}$
1	Styrene	874.9	889 (28°) <sup>23</sup> 878 (75°) <sup>22</sup>
2	$\alpha$ -Methylstyrene	963.5	
3	<i>p</i> -Methylstyrene	977.9	
4	2,3-Dihydroindene	1011.8	
5	Indene	1017.5	
6	<i>m</i> -Ethylstyrene	1064.4	
7	<i>p</i> -Ethylstyrene	1072.0	
8	1,3-Divinylbenzene	1086.0	
9	1,4-Divinylbenzene	1096.2	
10	1,2,3,4-Tetrahydronaphthalene	1125.6	

In order to identify all of the separated alkylbenzene degradation products, it was necessary to establish the Kováts retention indices of individual aromatics using incremental ( $\delta I$ ) values. As the availability of literature data for these calculations is inadequate, the experimental results, however, had to be found for different positions of substituents in the molecules (Table IV). The incremental values that were not determined experimentally, but were derived from literature data, are also indicated.

TABLE IV

INCREMENTAL  $\delta I$  VALUES OF SOME SUBSTITUENTS ON PHENYL

Column, silicone rubber SE-30; temperature, 65°.

No.	Functional group	Basis of calculation	$\delta I$	Note
1	-CH <sub>3</sub> (on phenyl)	$I_T - I_B$	102.8	
2	-CH <sub>2</sub> ·CH <sub>3</sub>	$I_{EB} - I_B$	194.3	
3	-CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>3</sub>	$I_{nPrB} - I_B$	283.3	
4	-CH·CH <sub>3</sub>	$I_{iPrB} - I_B$	255.3	
5	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \end{array}$	$I_{nBuB} - I_B$	382.6	
6	-CH <sub>2</sub> ·CH·CH <sub>3</sub>	$I_{iBuB} - I_B$	338.3	
7	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_3 \end{array}$	$I_{sec \cdot BuB} - I_B$	338.3	
8	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \\   \\ -\text{C} \cdot \text{CH}_3 \end{array}$	$I_{tert \cdot BuB} - I_B$	320.6	
9	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \end{array}$	$I_{nPeB} - I_B$	480.4	

(Continued on p. 682)

TABLE IV (continued)

No.	Functional group	Basis of calculation	$\delta I$	Note
10	$-\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$   $\text{CH}_3$ $\text{CH}_3$	$I_{\text{sec-PeB}} - I_{\text{B}}$	427.3	
11	$-\text{C}\cdot\text{CH}_2\cdot\text{CH}_3$   $\text{CH}_3$	$I_{\text{tert-PeB}} - I_{\text{B}}$	415.7	
12	$-\text{CH}_2-$ (chain)	$I_{\text{nPrB}} - I_{\text{EB}}$	89.0	
13	$-\text{CH}_2-\text{CH}_2-$ (chain)	$I_{\text{nDuB}} - I_{\text{EB}}$	188.3	
14	$-\text{CH}=\text{CH}_2$	$I_{\text{St}} - I_{\text{B}}$	220.1	
15	$-\text{C}=\text{CH}_2$   $\text{CH}_3$	$I_{\alpha\text{-MeSt}} - I_{\text{B}}$	308.6	
16	$-\text{CH}=\text{CH}\cdot\text{CH}_3$	$I_{\text{AllylB}} - I_{\text{B}}$	349.4	
17	$-\text{CH}_2\cdot\text{CH}=\text{CH}_2$	$I_{\text{AllylB}} - I_{\text{B}}$	274.5	
18	$-\text{CH}_3$ (double bond and primary C atom)	$I_{\text{AllylB}} - I_{\text{St}}$	129.3	$-\text{CH}=\text{CH}\leftarrow$
19	$-\text{CH}_3$ (double bond and sec.-C atom)	$I_{\alpha\text{-MeSt}} - I_{\text{St}}$	88.2	$-\text{CH}=\text{CH}_2$ ↑
20	$-\text{CH}_3$ (double bond and sec.-C atom)	Ref. 23	92.0	$-\text{CH}=\text{C}-\text{CH}_3$ ↑
21	$=\text{CH}_2$	$I_{\text{AllylB}} - I_{\text{EB}}$	80.2	
22	$-\text{CH}_3$ (o-)	$I_{\text{1Me-2EtB}} - I_{\text{EB}}$	114.1	
23	$-\text{CH}_3$ (m-)	$I_{\text{1Me-3EtB}} - I_{\text{EB}}$	99.1	
24	$-\text{CH}_3$ (p-)	$I_{\text{1Me-4EtB}} - I_{\text{EB}}$	99.1	
25	$-\text{CH}_2\cdot\text{CH}_3$ (o-)	$I_{\text{1,2-d1EtB}} - I_{\text{EB}}$	193.6	
26	$-\text{CH}_2\cdot\text{CH}_3$ (m-)	$I_{\text{1,3-d1EtB}} - I_{\text{EB}}$	182.4	
27	$-\text{CH}_2\cdot\text{CH}_3$ (p-)	$I_{\text{1,4-d1EtB}} - I_{\text{EB}}$	188.0	
28	$-\text{CH}=\text{CH}_2$ (o-)	$I_{\alpha\text{-MeSt}} - I_{\text{T}}$	233.0	
29	$-\text{CH}=\text{CH}_2$ (m-)	$I_{\text{m-MeSt}} - I_{\text{T}}$	217.6	
30	$-\text{CH}=\text{CH}_2$ (p-)	$I_{\text{p-MeSt}} - I_{\text{T}}$	220.2	
31	$-\text{CH}=\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$	$I_{\beta\text{-EtSt}} - I_{\text{B}}$	433.4	
32	$-\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_3$	$I_{\text{AllylB}} + \delta I_{-\text{CH}_3}$ (double bond and primary C atom)	403.8	Only by calculation; <i>cis</i> - and <i>trans</i> -forms
33	$-\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$	$I_{\text{nPrB}} + \delta I_{=\text{CH}_2}$	363.5	Only by calculation
34	$-\text{C}=\text{CH}\cdot\text{CH}_3$   $\text{CH}_3$	$I_{\alpha,\beta\text{-d1MeSt}} - I_{\text{B}}$	435.9	
35	$-\text{C}\cdot\text{CH}_2\cdot\text{CH}_3$    $\text{CH}_2$	$I_{\alpha\text{-EtSt}} - I_{\text{B}}$	403.6	
36	$-\text{CH}\cdot\text{CH}=\text{CH}_2$   $\text{CH}_3$	$I_{\text{PrB}} + \delta I_{=\text{CH}_2}$	335.5	Only by calculation
37	$-\text{CH}_2-\text{C}=\text{CH}_2$   $\text{CH}_3$	$I_{\beta\text{-MeAllylB}} - I_{\text{B}}$	367.6	
38	$-\text{CH}=\text{C}-\text{CH}_3$   $\text{CH}_3$	$I_{\text{AllylB}} + \delta I_{-\text{CH}_3}$ (see No. 20)	441.4	Only by calculation

The homeomorphism factors found for individual substituents permitted the calculation of retention indices for unavailable compounds. Both retention indices obtained from the sum of the incremental values of the indices of the parent compounds and experimentally determined indices are shown in Table V.

The calculated values of the retention indices of the compounds were related to their boiling points ( $T_b$ ) in order to confirm the proposed structures (Fig. 1).

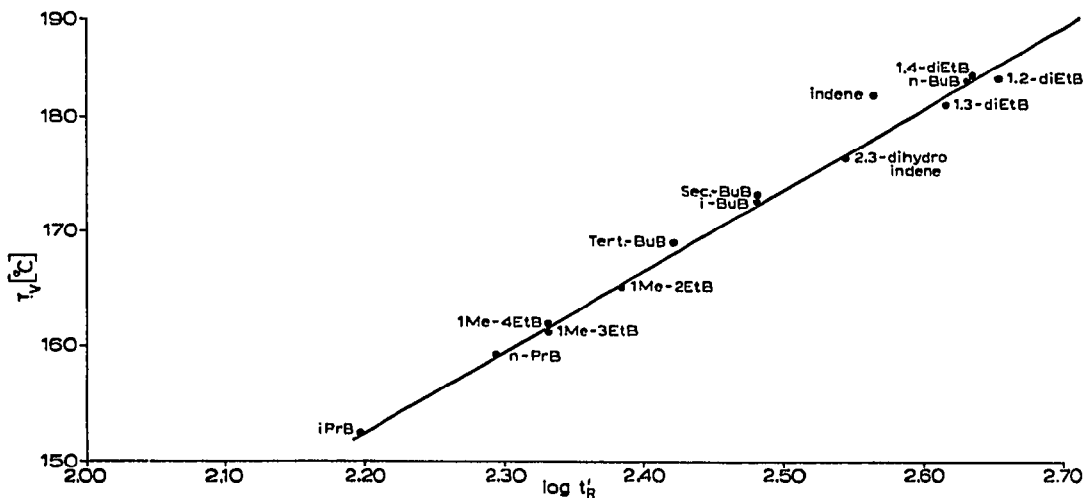


Fig. 1. Plot of  $T_b$  versus  $\log t'_R$ . Liquid phase: SE-30. Column temperature: 65°.

## DISCUSSION

The identification of thermal degradation products is a problem in pyrolysis gas chromatography because, owing to the very complex pyrolyzate composition, the possibility of identifying compounds from the retention data for pure components is very limited. In order to solve this problem, the Kováts retention indices were used.

For all available alkylbenzenes, either thermally treated or expected to be in the pyrolyzate, retention indices were determined on apolar stationary phases (squalane and SE-30), a stationary phase of medium polarity (tributyl citrate, Citroflex A-4) and a polar stationary phase (Carbowax 6000). The characteristic behaviour of the retention indices of the investigated alkylbenzenes on polar phases compared with apolar phases, expressed as  $\Delta I$ , show many regularities<sup>19</sup>, which will not be discussed in this paper.

For *m*- and *p*-xylenes on squalane as the stationary phase, we found the elution order to be in agreement with the results of Bonastre and Grenier<sup>7</sup> and Hively and Hinton<sup>20</sup>, *i.e.*, *p*-xylene is eluted before *m*-xylene. The opposite elution order (*m*-xylene before *p*-xylene) was found by Loewenguth and Tourres<sup>4</sup> and Schomburg<sup>25</sup>. All these workers used capillary and not packed columns.

The relationship between the increments,  $\delta I$ , of some individual substituents and their carbon numbers on silicone rubber SE-30 is illustrated in Fig. 2, where the straight lines for all saturated *n*-, *iso*-, *sec*- and *tert*-substituents are nearly parallel.

The change in the incremental values with the column temperature on certain

TABLE V

## KOVÁTS RETENTION INDICES OF SOME UNSATURATED AROMATIC COMPOUNDS

No.	Compound	Structure	$I_{65}^{SE-30}$ (calc.)	Basis of calculation	$I_{65}^{SE-30}$ (exptl.)	$I_{calc.} - I_{exptl.}$
1	Allylbenzene	<chem>Ph.CH2.CH=CH2</chem>	—	Plot of $T_0$ vs. $\log t'_R$	929.3	
2	Isoallylbenzene	<chem>Ph.CH=CH.CH3</chem>	—	Plot of $T_0$ vs. $\log t'_R$	1004.2	
3	$\alpha$ -Methylstyrene	<chem>Ph.C=CH2</chem> <chem>CH3</chem>	963.4	$I_B + \delta I_{-C=CH_2}$	963.1	+0.3
4	1-Methyl-2-vinylbenzene	<chem>CH3</chem> <chem>C1=CC=C(C=C1)C=C</chem>	989.0	$I_{St} + \delta I_{-CH_3 o}$	990.6	-1.6
5	1-Methyl-3-vinylbenzene	<chem>CH3</chem> <chem>C1=CC=C(C=C1)C=C</chem>	974.0	$I_{St} + \delta I_{-CH_3 m}$	973.2	+0.8
6	1-Methyl-4-vinylbenzene	<chem>CH3</chem> <chem>C1=CC=C(C=C1)C=C</chem>	974.0	$I_{St} + \delta I_{-CH_3 p}$	977.6	-3.6
7	$\beta$ -Ethylstyrene	<chem>Ph.CH=CH.CH2.CH3</chem>	1093.2	$I_{-AllylB} + \delta I_{-CH_2}$ (chain)	1098.2	-5.0
8	$\gamma$ -Methylallylbenzene	<chem>Ph.CH2.CH=CH.CH3</chem>	1058.6	$I_{AllylB} + \delta I_{-CH_3}$ (double bond, primary C atom)	—	
9	4-Phenyl-1-butene	<chem>Ph.CH2.CH2.CH=CH2</chem>	1018.3	$I_{pRB} + \delta I_{-CH_2}$	—	
10	$\alpha$ -Ethylstyrene	<chem>Ph.C=CH2</chem> <chem>CH2=CH2</chem>	1054.6	$I_{St} + \delta I_{-CH_2, CH_3}$	1058.4	-3.8
			1063.2	$I_{\alpha-MeSt} + \delta I_{-CH_3}$	—	+4.8
11	$\alpha, \beta$ -Dimethylstyrene	<chem>Ph.C=CH.CH3</chem> <chem>CH3</chem>	1092.4	$I_{-AllylB} + \delta I_{-CH_3}$ (double bond, sec.-C atom)	1090.7	+1.7
12	$\alpha$ -Methylallylbenzene	<chem>Ph.C=CH=CH2</chem> <chem>CH3</chem>	990.3	$I_{t-pRB} + \delta I_{=CH_2}$	—	
13	$\beta$ -Methylallylbenzene	<chem>Ph.CH2.C=CH2</chem> <chem>CH3</chem>	1021.3	$I_{AllylB} + \delta I_{-CH_3}$ (ref. 23)	1022.4	-1.1
14	$\beta$ -Methylisoallylbenzene	<chem>Ph.CH=C.CH3</chem> <chem>CH3</chem>	1096.2	$I_{t-AllylB} + \delta I_{-CH_3}$ (ref. 23)	—	
15	2-Ethylstyrene	<chem>CH3</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1068.4	$I_{St} + \delta I_{-CH_2, CH_3 o}$	1086.4	-18.0
			1082.1	$I_{EB} + \delta I_{-CH=CH_2 o}$	—	-4.3
16	3-Ethylstyrene	<chem>CH=CH2</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1057.3	$I_{St} + \delta I_{-CH_2, CH_3 m}$	1063.9	-6.6
			1075.4	$I_{EB} + \delta I_{-CH=CH_2 m}$	—	+11.5
17	4-Ethylstyrene	<chem>CH2=CH3</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1062.9	$I_{St} + \delta I_{-CH_2, CH_3 o}$	1071.7	-8.8
			1069.3	$I_{EB} + \delta I_{-CH=CH_2 o}$	—	-2.4
18	1,3-Divinylbenzene	<chem>CH=CH2</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1092.5	$I_{St} + \delta I_{-CH=CH_2 m}$	1085.2	+7.3
19	1,4-Divinylbenzene	<chem>CH=CH2</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1095.1	$I_{St} + \delta I_{-CH=CH_2 p}$	1095.9	+0.8
20	1-Methyl-2-isoallylbenzene	<chem>CH=CH2</chem> <chem>CH=CH2</chem> <chem>C1=CC=C(C=C1)C=C</chem>	1118.3	$I_{t-AllylB} + \delta I_{-CH_3 o}$	1116.5	+1.7



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21	1-Methyl-3-isoallylbenzene		1103.3	$I_{1,3\text{-AllylB}} + \delta I_{\text{-CH}_3 \text{ m-}}$	1102.3	+1.0
22	1-Methyl-4-isoallylbenzene		1103.3	$I_{1,4\text{-AllylB}} + \delta I_{\text{-CH}_3 \text{ p-}}$	1104.2	-0.9
23	1-Methyl-2-α-methylstyrene		1077.2	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ o-}}$	1061.0	+1.2
24	1-Methyl-3-α-methylstyrene		1062.2	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ m-}}$	1066.3	-4.1
25	1-Methyl-4-α-methylstyrene		1062.2	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ p-}}$	1069.1	-6.9
26	1-Methyl-2-allylbenzene		1043.4	$I_{\text{AllylB}} + \delta I_{\text{-CH}_3 \text{ o-}}$	-	-
27	1-Methyl-3-allylbenzene		1028.4	$I_{\text{AllylB}} + \delta I_{\text{-CH}_3 \text{ m-}}$	1028.0	+0.4
28	1-Methyl-4-allylbenzene		1028.4	$I_{\text{AllylB}} + \delta I_{\text{-CH}_3 \text{ p-}}$	1033.3	-4.9
29	1,2-Dimethyl-3-vinylbenzene		1111.9	$I_{1,2\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ o-}}$	1097.1	+14.8
			1096.5	$I_{1,2\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ m-}}$	-	-0.6
			1104.7	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ o-}}$	-	+7.6
			1089.7	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ m-}}$	-	-7.4
			1100.7*		-	+2.9*
30	1,3-Dimethyl-4-vinylbenzene		1090.8	$I_{1,3\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ o-}}$	1079.8	+11.0
			1078.0	$I_{1,3\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ p-}}$	-	-1.8
			1089.7	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ m-}}$	-	+9.9
			1089.7	$I_{\alpha\text{-MeSt}} + \delta I_{\text{-CH}_3 \text{ p-}}$	-	+9.9
31	1,2-Dimethyl-4-vinylbenzene		1087.0*		-	+7.5*
			1099.1	$I_{1,2\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ p-}}$	1099.9	-0.8
			1096.5	$I_{1,2\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ m-}}$	-	-3.4
			1087.3	$I_{\text{m-MeSt}} + \delta I_{\text{-CH}_3 \text{ o-}}$	-	-12.6
			1072.3	$I_{\text{m-MeSt}} + \delta I_{\text{-CH}_3 \text{ p-}}$	-	-27.6
32	1,3-Dimethyl-5-vinylbenzene		1088.8*		-	-11.1*
			1075.4	$I_{1,3\text{-DiMeB}} + \delta I_{\text{-CH=CH}_2 \text{ m-}}$	1072.9	+2.5
			1073.1	$I_{\text{St}} + 2\delta I_{\text{-CH}_3 \text{ m-}}$	-	+0.2
			1072.3	$I_{\text{m-MeSt}} + \delta I_{\text{-CH}_3 \text{ m-}}$	-	-0.6
			1073.6*		-	+0.7*

(Continued on p. 686)

TABLE V (continued)

No.	Compound	Structure	$I_{65}^{SE-30}$ (calc.)	Basis of calculation	$I_{65}^{SE-30}$ (exptl.)	$I_{calc.} - I_{exptl.}$
33	1,4-Dimethyl-2-vinylbenzene		1075.4 1090.8 1089.7 1087.3 1085.8*	$I_{1,4-dimEB} + \delta I_{-CH=CH_2, m-}$ $I_{1,4-dimEB} + \delta I_{-CH=CH_2, o-}$ $I_{o-MeSt} + \delta I_{-CH_3, p-}$ $I_{o-MeSt} + \delta I_{-CH_3, o-}$	1075.8	-0.4 +15.0 +13.9 +11.5
34	1,3-Dimethyl-2-vinylbenzene		1090.8 1104.7	$I_{1,3-dimEB} + \delta I_{-CH=CH_2, o-}$ $I_{o-MeSt} + \delta I_{-CH_3, o-}$	1117.9	+10.0* -27.1 -13.2
35	1-Vinyl-3-isopropylbenzene		1127.7	$I_{IPrB} + \delta I_{-CH=CH_3, m-}$	1117.4	+10.3
36	1-Vinyl-4-isopropylbenzene		1130.3	$I_{IPrB} + \delta I_{-CH=CH_2, p-}$	1136.5	-6.2
37	1-Vinyl-3α-methylstyrene		1181.0	$I_{o-MeSt} + \delta I_{-CH=CH_3, m-}$	1195.8	-14.8
38	1-Vinyl-4α-methylstyrene		1183.6	$I_{o-MeSt} + \delta I_{-CH=CH_2, p-}$	1218.5	-34.9

\*Mean values.

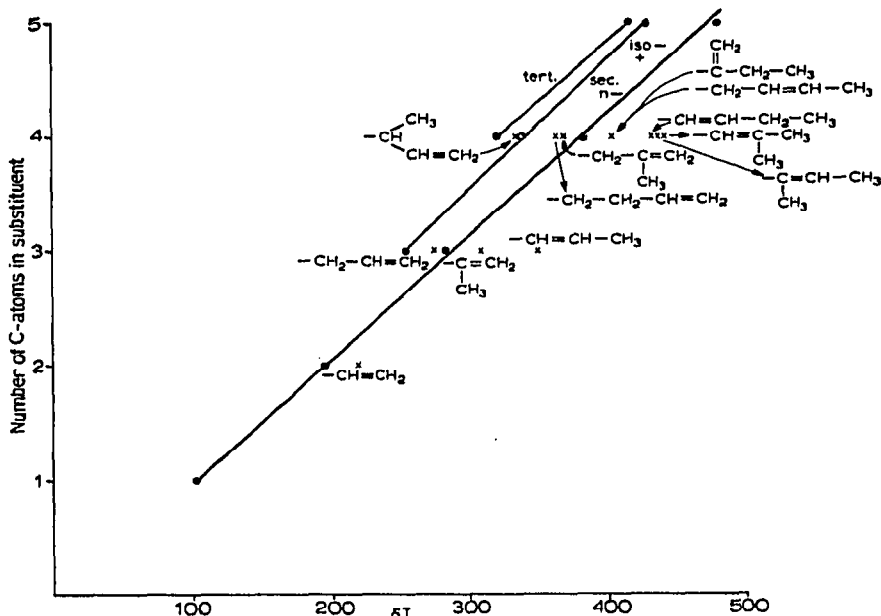


Fig. 2. Dependence of incremental  $\delta I$  values on carbon number for saturated (●) and unsaturated (×) substituents.

liquid phases is represented in Fig. 3, including the results obtained by Cook and Raushel<sup>16</sup>. The relationship is linear with some discrepancies for smaller groups at column temperatures of 100° and 130°.

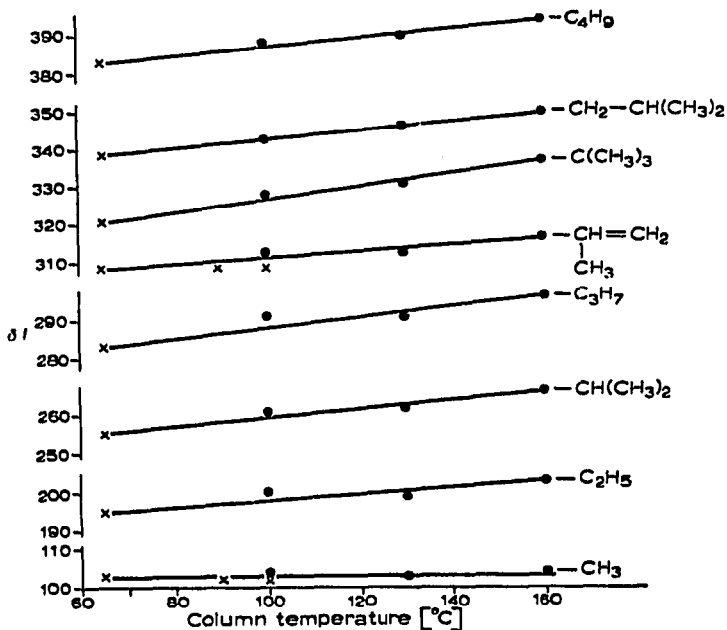


Fig. 3. Relationship between incremental  $\delta I$  values and column temperature on silicone rubber SE-30. ●, Results from ref. 16; ×, results from this work.

Some retention indices can be determined on different bases, depending on the component taken as the parent compound. The retention index of 1,2-dimethyl-3-vinylbenzene, for example, could be calculated with *o*-xylene or *o*-methylstyrene as the parent compound by adding the incremental values of the corresponding substituents. As seen in Table V, the results obtained with different parent compounds are similar. Therefore, the average value of the retention indices for each compound obtained was taken as the final value. Table V also shows that the compounds with *ortho*- and *vicinal*-substitution show the greatest difference between calculated and experimental values. These differences can amount to almost 27 units (1,3-dimethyl-2-vinylbenzene), while for other isomers they will not be higher than approximately 11 index units. This implies a very important influence and interaction between substituents on an aromatic ring and it is therefore of great importance to determine increments for different substituent positions when retention index values are being calculated.

An interesting example of the differences between calculated and experimental values is the case of *m*- and *p*-dialkylbenzenes with a methyl group as one of the substituents. These isomers are separated from each other on the column but the calculated retention indices obtained from  $\delta I_{-CH_3}$  values are the same, based on values for  $I_{1Me-3EtB}$  and  $I_{1Me-4EtB}$ , which refer to compounds that do not separate on the column used.

Regardless of certain deviations in the results found for a large number of different alkylbenzene and alkenylbenzene isomers, the differences between experimental and calculated values are not very great and can be used for the unambiguous identification of alkylbenzene degradation products. The most important fact is that the incremental values that are used for calculation can be obtained from measurements made on compounds with structures as similar as possible to that of the examined compound. Only then will the result obtained be sufficiently close to the actual value. Using alkanes as an example, Ladon<sup>26</sup> showed that the influence of the intramolecular environment is very important, and the contribution of a structural element to the retention index is a function of the total intramolecular environment. While different environments in particular molecules will contribute to different interactions with identical structural elements, the calculation of exact values of absolute retention times or indices will always be limited to some extent.

## CONCLUSION

Kováts retention indices of more than 50 alkylbenzenes and related aromatics on squalane, silicone rubber SE-30, Citroflex A-4 and Carbowax 6000 were determined. By means of these results, the homeomorphism factors,  $\delta I$ , for a number of different structural elements were found and used in order to obtain retention indices for numerous aromatic compounds expected to be present in the degradation products of alkylbenzenes. The results obtained can be used satisfactorily for the identification of pyrolysis products, including similar isomers.

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