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OPEN TUBULAR COLUMN GAS CHROMATOGRAPHY OF  
DEHYDROGENATION PRODUCTS OF C<sub>6</sub>-C<sub>10</sub> *n*-ALKANESSEPARATION AND IDENTIFICATION OF MIXTURES OF C<sub>6</sub>-C<sub>10</sub>  
STRAIGHT-CHAIN ALKANES, ALKENES AND AROMATICS

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## SUMMARY

A gas chromatographic method for the analysis of dehydrogenation products of C<sub>6</sub>-C<sub>10</sub> alkanes has been developed. The optimum working temperatures for the separation on a 200 m squalane column were determined. The analysis of approx. sixty components in the products, at 115°, takes about 170 min.

The retention indices of straight-chain alkenes and aromatics, C<sub>6</sub>-C<sub>10</sub>, of the dehydrogenation products on squalane were measured at temperatures of 86 and 115°. The changes of retention indices with temperature were calculated on the basis of the data. It was found out that aromatic hydrocarbons exhibit the greatest change of  $10 \cdot \delta I / \delta T = 2.0-2.9$ , followed by the *cis*-alkenes (0.2-0.4), while the retention indices of the *trans*-alkenes vary much less. Thus by varying the column temperature it is possible to change the selectivity for the separation of aromatics, alkenes and alkanes side by side, and also to vary the selectivity of the *cis/trans* alkenes separation. These relationships have been used for the identification of products. The structural increments  $H^s$  were calculated from the retention indices determined. It was found that the structural increment in the region of C<sub>6</sub>-C<sub>10</sub> *n*-alkenes depends upon the number of C atoms in the molecule and the column temperature. These characteristic functions can be applied to the identification of higher molecular compounds than the C<sub>10</sub> alkenes.

## INTRODUCTION

Normal alkanes separated from petroleum fractions by means of molecular sieves are used as the raw material for catalytic dehydrogenation. The products of dehydrogenation can contain practically all theoretically possible straight-chain alkenes, aromatic hydrocarbons and amounts of unreacted *n*-alkanes. The analytical problem, besides the satisfactory separation of the constituents, concerns their identification, because standards are lacking for some of the aromatics as well as for many of the alkenes. Likewise the retention data published so far for this field are far from complete.

Squalane is used mostly as the stationary phase for the separation of hydrocarbons. The hydrocarbons are eluted from the squalane column approximately in

the sequence of their boiling points. This facilitates their identification. Since the boiling points of the isomeric alkenes, having the same number of carbon atoms in the molecule, are very close and it is also necessary to consider the presence of the aromatics and the residual *n*-alkanes, the demands on the resolving power of the column for the separation of the dehydrogenation products are rather heavy. The use of effective open tubular columns for the separation of these multicomponent mixtures is an inevitable condition, because small structural deviations are only manifested in measurable differences of retention data in the case of highly effective columns.

## EXPERIMENTAL

The gas chromatograph Chrom-3, having a flame ionisation detector, was used. The capillary column of 200 m length and 0.2 mm inside diameter was coated with squalane by the dynamic method. The theoretical efficiency for ethylbenzene was found with an inlet pressure of N<sub>2</sub> carrier gas of 4 kp/cm<sup>2</sup>, a column temperature of 115° and a capacity ratio  $k = 1.4$  to be  $n = 375\,000$  and the effective efficiency to be  $N = 125\,000$  plates.

Complete retention indices on squalane for straight-chain alkenes have only been published up to alkenes having 8 C atoms in the molecule<sup>1</sup>. For C<sub>9</sub> and C<sub>10</sub> alkenes the retention data are incomplete or they are quoted as structural increments,  $H^s$  (ref. 2).

The identification of C<sub>6</sub>-C<sub>8</sub> alkenes was done by comparison of the retention indices determined with literature data. The straight-chain C<sub>9</sub> and C<sub>10</sub> alkenes were determined from the structural increments found for C<sub>6</sub>-C<sub>8</sub> alkenes. A polyethylene glycol column was used<sup>3</sup> for the identification of aromatics.

## RESULTS AND DISCUSSION

### *Separation with a squalane column*

The published retention data for squalane and straight-chain alkenes having the double bond between the 3 and 5 carbon atoms, show very near or equal values. In such cases a good gas chromatographic separation can only be performed with columns having maximum separation efficiency. It is for this reason that an open tubular column of 200 m length was used for the separation of the dehydrogenation products.

Even though squalane is considered as a nonpolar phase, the effect of column temperature upon the separation selectivity has been noticed. SANDERS AND MAYNARD<sup>4</sup> reported that at lower temperatures on a squalane column the retention times of the C<sub>4</sub>-C<sub>6</sub> alkenes can increase and the retention time of benzene decreases with respect to the corresponding alkanes. HIVELY AND HINTON<sup>5</sup> demonstrated that the variations of the retention indices with temperature on squalane are functions of the minimum cross-sectional area of the molecule. These values indicate that a separation of the dehydrogenation products with a squalane column at diverse temperatures will be convenient.

The chromatograms of the dehydrogenation products, which were concentrated by the FIA method according to the amount of alkenes and aromatics, were determined at temperatures of 86° and 115° and are shown in Fig. 1. The problem of the separation of the aromatics, already identified with the polyethylene glycol column, from the alkenes and alkanes was first investigated.

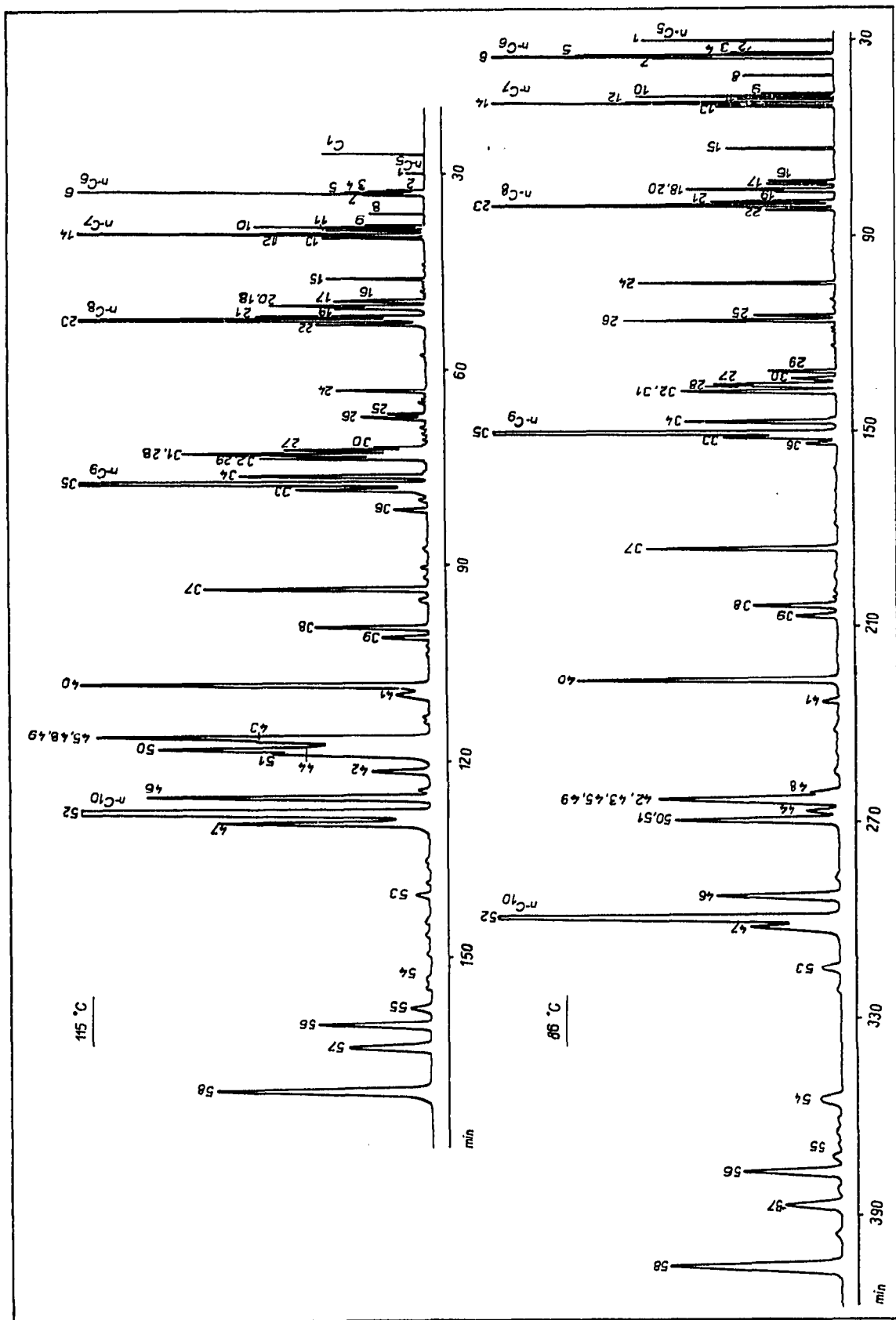


Fig. 1. Chromatograms of dehydrogenation products of C<sub>6</sub>-C<sub>10</sub> n-alkanes. Gas chromatograph Chrom-3 with flame ionisation detector. Column 200 m x 0.2 mm I.D. coated with squalane. Column temperature 86 and 115°. Sample size 1 µl, split 1/300. Carrier gas N<sub>2</sub>, inlet pressure 4 kp/cm<sup>2</sup>. Peaks, see Table I.

TABLE I

RETENTION INDICES OF STRAIGHT-CHAIN ALKENES AND C<sub>6</sub>-C<sub>10</sub> AROMATICS OF DEHYDROGENATION PRODUCTS DETERMINED ON A SQUALANE COLUMN AT 86 AND 115°

Peak number	Component	Boiling point (°C)	I <sub>86</sub> <sup>s</sup>	I <sub>115</sub> <sup>s</sup>	10 · $\frac{\delta I^s}{\delta T}$
1	<i>n</i> -Pentane	36.07	500.0	500.0	0.0
2	1-Hexene	63.48	583.1	584.0	0.3
3	<i>trans</i> -3-Hexene	67.08	591.4	590.6	-0.3
4	<i>cis</i> -3-Hexene	66.45	593.0	593.7	0.2
5	<i>trans</i> -2-Hexene	67.88	596.7	596.4	-0.1
6	<i>n</i> -Hexane	68.74	600.0	600.0	0.0
7	<i>cis</i> -2-Hexene	68.89	604.6	605.4	0.2
8	Benzene	80.10	646.6	653.6	2.4
9	1-Heptene	93.64	682.8	683.5	0.2
10	<i>trans</i> -3-Heptene	95.67	687.5	687.4	0.0
11	<i>cis</i> -3-Heptene	95.75	691.7	692.3	0.2
12	<i>trans</i> -2-Heptene	97.95	698.7	698.7	0.0
13	<i>cis</i> -2-Heptene	98.41	704.3	705.1	0.3
14	<i>n</i> -Heptane	98.43	700.0	700.0	0.0
15	Toluene	110.63	754.2	760.7	2.2
16	1-Octene	121.28	782.3	782.9	0.2
17	<i>trans</i> -4-Octene	122.25	784.2	784.1	0.0
18	<i>cis</i> -4-Octene	122.54	787.9	788.6	0.2
19	<i>cis</i> -3-Octene	122.90	789.5	790.2	0.2
20	<i>trans</i> -3-Octene	123.30	788.4	788.0	-0.1
21	<i>trans</i> -2-Octene	125.00	797.7	797.3	-0.1
22	<i>cis</i> -2-Octene	125.64	802.8	803.6	0.3
23	<i>n</i> -Octane	125.66	800.0	800.0	0.0
24	Ethylbenzene	136.19	844.3	851.3	2.4
25	<i>p</i> -Xylene	138.35	858.1	864.9	2.3
26	<i>m</i> -Xylene	139.10	860.3	866.3	2.3
27	<i>trans</i> -4-Nonene	(144)	884.2	884.4	0.0
28	<i>cis</i> -4-Nonene	(144)	884.8	886.0	0.4
29	<i>o</i> -Xylene	144.41	880.1	888.1	2.7
30	1-Nonene	146.86	882.2	882.8	0.2
31	<i>trans</i> -3-Nonene	(147.9)	886.6	886.5	0.0
32	<i>cis</i> -3-Nonene	(147.9)	887.0	888.1	0.4
33	<i>cis</i> -2-Nonene	148.50	901.5	902.6	0.4
34	<i>trans</i> -2-Nonene	—	896.6	896.6	0.0
35	<i>n</i> -Nonane	150.80	900.0	900.0	0.0
36	Isopropylbenzene	152.39	903.5	910.8	2.5
37	<i>n</i> -Propylbenzene	159.22	932.6	940.2	2.6
38	<i>m</i> -Ethyltoluene	161.31	945.6	952.1	2.2
39	<i>p</i> -Ethyltoluene	161.99	948.0	955.1	2.4
40	<i>o</i> -Ethyltoluene	165.15	961.2	968.8	2.6
41	1,3,5-Trimethylbenzene	164.92	965.3	971.2	2.0
42	1,2,4-Trimethylbenzene	169.35	982.2	990.4	2.8
43	<i>cis</i> -4-Decene	(170.5)	982.2	983.4	0.4
44 <sup>n</sup>	<i>trans</i> -4-Decene	(170.5)	982.2	982.7	0.2
45	1-Decene	170.57	982.2	982.7	0.2
46	<i>trans</i> -2-Decene	(170.6)	996.7	996.6	0.0
47	<i>cis</i> -2-Decene	(170.6)	1001.2	1002.2	0.3
48	<i>cis</i> -5-Decene	(170.7)	981.0	982.1	0.4
49 <sup>n</sup>	<i>trans</i> -5-Decene	(171.3)	984.0	984.7	0.2
50	<i>trans</i> -3-Decene	(173.3)	985.4	985.5	0.0
51	<i>cis</i> -3-Decene	(173.3)	985.4	986.4	0.3
52	<i>n</i> -Decane	174.12	1000.0	1000.0	0.0
53	1,2,3-Trimethylbenzene	176.08	1007.5		

<sup>n</sup> Identified on the basis of dehydrogenation mechanism.

TABLE I (continued)

Peak number	Component	Boiling point (°C)	I <sub>86</sub> <sup>s</sup>	I <sub>115</sub> <sup>s</sup>	10 · $\frac{\delta I^s}{\delta T}$
54	1,3-Diethylbenzene	181.10	1025.0		
55	1-m-3-n-Propylbenzene	181.80	1030.5	1037.1	2.3
56	n-Butylbenzene	183.27	1033.0	1040.0	2.4
57	1,2-Diethylbenzene	183.75	1036.0	1043.6	2.6
58	1-m-2-n-Propylbenzene	184.80	1042.0	1050.5	2.9
59	1,3-Dimethyl-4-ethylbenzene	188.41		1070.8	
60	n-Undecane	195.89	1100.0	1100.0	0.0

TABLE II

STRUCTURAL INCREMENTS H<sup>s</sup> OF STRAIGHT-CHAIN C<sub>6</sub>-C<sub>10</sub> ALKENES ON SQUALANE AT TEMPERATURES OF 86 AND 115°

Component	Structural increment H <sup>s</sup>		10 · $\frac{\delta I^s}{\delta T}$
	86°	115°	
1-Hexene	-16.9	-16.0	0.3
1-Heptene	-17.2	-16.5	0.2
1-Octene	-17.7	-17.1	0.2
1-Nonene	-17.8	-17.2	0.2
1-Decene	-17.8	-17.3	0.2
<i>trans</i> -2-Hexene	- 3.3	- 3.6	-0.1
<i>trans</i> -2-Heptene	- 1.3	- 1.3	0.0
<i>trans</i> -2-Octene	- 2.3	- 2.7	-0.1
<i>trans</i> -2-Nonene	- 3.4	- 3.4	0.0
<i>trans</i> -2-Decene	- 3.3	- 3.3	0.0
<i>cis</i> -2-Hexene	4.7	5.4	0.2
<i>cis</i> -2-Heptene	4.3	5.1	0.3
<i>cis</i> -2-Octene	2.8	3.6	0.3
<i>cis</i> -2-Nonene	1.5	2.6	0.4
<i>cis</i> -2-Decene	1.2	2.2	0.3
<i>trans</i> -3-Hexene	- 8.6	- 9.4	-0.3
<i>trans</i> -3-Heptene	-12.5	-12.6	0.0
<i>trans</i> -3-Octene	-11.6	-12.0	-0.1
<i>trans</i> -3-Nonene	-13.4	-13.5	0.0
<i>trans</i> -3-Decene	-14.6	-14.5	0.0
<i>cis</i> -3-Hexene	- 7.0	- 6.3	0.2
<i>cis</i> -3-Heptene	- 8.3	- 7.7	0.2
<i>cis</i> -3-Octene	-10.5	- 9.8	0.2
<i>cis</i> -3-Nonene	-13.0	-11.9	0.4
<i>cis</i> -3-Decene	-14.6	-13.6	0.3
<i>trans</i> -4-Octene	-15.8	-15.9	0.0
<i>trans</i> -4-Nonene	-15.9	-15.6	0.1
<i>trans</i> -4-Decene	-17.8	-17.3	0.2
<i>cis</i> -4-Octene	-12.1	-11.4	0.2
<i>cis</i> -4-Nonene	-15.2	-14.0	0.4
<i>cis</i> -4-Decene	-17.8	-16.6	0.4
<i>trans</i> -5-Decene	-16.0	-15.3	0.2
<i>cis</i> -5-Decene	-19.0	-17.9	0.4

The aromatics benzene and toluene are separated in the temperature range investigated (86 and 115°) from the other constituents. The separation problems begin at *o*-xylene, which at a temperature of 86° elutes immediately before the nonenes. With an increase in the column temperature the retention of *o*-xylene is shifted into the nonenes and at a temperature of 115° it is eluted immediately behind *cis*-3-nonene. In the separation of aromatic C<sub>9</sub> hydrocarbons the effect of temperature is manifested in the separation of isopropylbenzene from *cis*-2-nonene, and possibly from *n*-nonane. Temperatures of 86° and higher are favourable for the separation. At 86°, of the remaining theoretically possible C<sub>9</sub> aromatics 1,2,4-trimethylbenzene, *sec.*-butylbenzene and isobutylbenzene can elute in the decene zone. By increasing the column temperature to 115° they will be shifted between *cis*-3-decene and *trans*-2-decene. The separation of C<sub>10</sub> aromatics does not present a problem, because the dehydrogenated mixture does not contain undecenes.

The column temperature also affects the separation of the individual alkenes to a smaller extent, and sometimes their separation from the *n*-alkanes. Among the straight-chain C<sub>6</sub>-C<sub>9</sub> alkenes the following two pairs, *trans*-3-octene + *cis*-4-octene and *trans*-3-nonene + *cis*-3-nonene, are not even partly separated, at a column temperature of 86°. In the case of the straight-chain decenes a common peak is observed for *trans*-3-decene + *cis*-3-decene and *trans*-4-decene + *cis*-4-decene + 1-decene. The separation of these unseparated alkenes can partly be achieved by adjustment of the column temperature. The separation of *cis*-4-octene from *trans*-3-octene was obtained at a column temperature below 65°; the separation of all nonenes, even in the presence of *o*-xylene, was obtained at a temperature of 92°, and at the temperature of 115° *cis*-3-decene was separated from *trans*-3-decene and *cis*-4-decene from the common peak for 1-decene + *trans*-4-decene + *cis*-5-decene. The only information which was not ascertained, out of the 33 theoretically possible straight-chain C<sub>6</sub>-C<sub>10</sub> alkenes, were data for 1-decene and *trans*-4-decene.

The problems of *n*-alkane separation from straight-chain alkenes on squalane are substantially those concerning the separation of *cis*- and *trans*-2-alkenes from the corresponding *n*-alkanes. The separation is affected by the working temperature of the column. Higher column temperatures are preferable for the separation of *cis*-2-alkenes from *n*-alkanes.

#### *Identification of straight-chain alkenes*

The retention indices were calculated out of the chromatograms determined for the dehydrogenation products at temperatures of 86 and 115°. Comparison of measured and tabulated data of the structural increments  $H^s$  and the variations of retention indices with temperature were used for the identification. The numbering of the identified chromatographic peaks, the boiling points, the retention indices and their variations with temperature are shown in Table I. Some interesting correlations can be deduced.

#### *Effect of the carbon chain length upon the structural increment $H^s$*

The structural increments  $H^s$  for the straight-chain C<sub>6</sub>-C<sub>8</sub> alkenes, which had been calculated from the retention indices, indicated a certain dependence on the number of C atoms. Table II presents these stated values of the structural increments at temperatures of 86 and 115° for the individual groups of straight-chain alkenes.

A certain deviation is found for *trans*-2-hexene, *trans*-3-heptene and *trans*-4-octene.

The correlations found permit the determination of the values for the structural increments, and consequently the values of the retention indices for straight-chain alkenes having a higher number of C atoms per molecule than 10 can also be found.

*Squalane column temperature: effect upon the retention index of straight-chain alkenes*

From the chromatograms determined with the squalane column (Fig. 1) it can be seen that at different temperatures a number of different kinds of peaks were recorded and a shift of some peaks was also noticed. This result demonstrates the variation of the relative retention of some of the dehydrogenation products according to the column temperature. The corresponding variations of the retention indices with temperature for the various constituents are given in Table I. The greatest variations were found for the aromatics ( $10 \cdot \delta I / \delta T = 2.0-2.9$ ). The values for *cis*-alkenes and 1-alkenes correspond approximately to one tenth of this value (e.g. 0.2-0.4). The retention indices of the *trans*-alkenes are practically temperature independent. The variation of the retention indices for the individual alkenes are given in Table II.

Considering that under the given conditions 0.6 index units are sufficient for the resolution of two constituents, by varying the column temperature by 20° it is possible to obtain the partial separation of *cis-trans* isomers, whose peaks generally overlap. The retention of *cis*-alkenes, relative to the corresponding *trans*-isomers, can be extended by raising the temperature of the squalane column. The temperature effect upon the separation selectivity for the *cis/trans* alkenes is demonstrated in Table III. The differences in the retention indices found by the subtraction of the indices for *trans*-alkenes from the *cis*-isomers are compared for alkenes having a similar position of the double bond.

TABLE III

DIFFERENCES IN THE RETENTION INDICES OF THE *cis*- AND *trans*-ALKENES AT TEMPERATURES OF 86 AND 115°

No. of carbon atoms	2-Alkenes		3-Alkenes		4-Alkenes		5-Alkenes	
	86°	115°	86°	115°	86°	115°	86°	115°
C <sub>6</sub>	7.9	9.0	1.6	3.1	—	—	—	—
C <sub>7</sub>	5.6	6.4	4.2	4.9	—	—	—	—
C <sub>8</sub>	5.1	6.3	1.1	2.2	3.7	4.5	—	—
C <sub>9</sub>	4.8	5.9	0.0	1.6	0.7	1.6	—	—
C <sub>10</sub>	4.5	5.5	0.0	0.9	0.0	0.7	3.0	-2.6

The effect of temperature on the squalane column is even more expressive in the case where aromatics are to be separated together with alkenes. The variations of retention indices for the aromatics, compared with those of the straight-chain alkenes, are approximately ten times higher. That means that by varying the column temperature (at which the peaks for the alkenes and aromatics overlap) by about 2° or 3° a partial separation can be obtained.

In this way, the knowledge of the variations of the retention indices with temperature permits the calculation of the optimum temperature for the separation of the constituents of a mixture. It also serves for the identification of unknown components.

*Dependence of straight-chain alkenes retention indices upon the boiling point*

The comparison of the boiling points and the corresponding retention indices of straight-chain  $C_6$ – $C_8$  alkenes and alkanes on the squalane column indicates that at  $40^\circ$  the boiling point does not follow the retention index in the case of the following pairs: *cis*-3-hexene and *trans*-3-hexene, *cis*-2-heptene and *n*-heptane, *cis*-2-octene and *n*-octane. It is necessary to mention that at this temperature the other *cis*-alkenes are retained by the squalane column longer than would correspond to the differences between the boiling points of the *trans*-alkenes, or possibly of the *n*-alkanes. By raising the temperature of the column to  $115^\circ$  this difference increases. The retention indices of the aromatic  $C_6$ – $C_{10}$  hydrocarbons at a temperature of  $86^\circ$  fulfil approximately the sequence of the boiling points of the other constituents in the dehydrogenation product. Raising the column temperature transfers the aromatics into the zone of higher boiling alkenes. At a lower temperature the opposite is valid.

The retention indices found and the known boiling points of straight-chain alkenes were used for verification of the Kováts equation defining the relationship between the retention index and the boiling point of the components ( $\delta I = 5\delta t_b$ ). Good agreement was only obtained for geometrically similar *trans-trans* and *cis-cis* isomers (approx. about one unity of index). The equation was found to be more reliable with an increase of C atoms in the molecule.

The constant of proportionality calculated from the retention indices and corresponding boiling points indicates a certain dependence for  $C_6$ – $C_8$  alkenes. On the basis of this dependence and the known boiling points of 1-nonene and 1-decene, the boiling points for the remaining nonenes and decenes can be calculated; in Table I these are given in parentheses as approximate values. More details will be published in future papers.

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