

Gas Chromatographic Analysis of the Products of Hydroisomerization of C₈-Aromates on a Capillary Column Coated with Squalane

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A reaction mixture of hydroisomerization of C₈-aromates containing some 60 hydrocarbons has been analyzed on squalane at 49 and 55°C using reference compounds and elution data known in the literature. A linear function of the calculated elution indices *vs.* boiling points of the aromates, cyclanes, and C₈-alkanes was obtained. Compared to the elution indices of the C₈-alkanes, the elution indices of the C₈-cyclanes and those of the C₈-aromates are higher by 10 and lower by 5 index units, respectively.

Hydroisomerization of C₈-aromates, a process similar by its working conditions to reformation, produces a reaction mixture containing, in addition to aromates, cyclanes and alkanes. The separation of C₈-aromates has been one of the most frequently occurring problems in gas chromatography on packed columns [1–4]. Identification of hydrocarbons in gasolines after reformation has been reported [5–10]. As some of these works show only obtained chromatograms and no elution data, their character is merely informative.

Apart from the thermodynamical stability of C₇–C₁₀ alkylcyclopentanes and alkylcyclohexanes the Soviet workers [11–16] have studied also the separation of these substances on capillary columns. *Makarova et al.* [11] have described the separation of C₈-methylethylcyclopentanes in a mixture with *n*-propylcyclopentane and isopropylcyclopentane on dibutyltetrachlorophthalate, a phase capable of separating these isomers. This work does not contain, however, the elution data of the individual alkylcyclopentanes. The separation of C₇–C₈ naphthenes on squalane has been reported by *Zacharenko et al.* [12] who give also the elution data relative to *n*-hexane.

Sidorov [17], investigating the relation between the relative elution times and the boiling points of naphthenes and C₅–C₈ alkanes on capillary columns coated with squalane, vacuum oil VM-4, tricresylphosphate and polyethyleneglycol 600, came to the conclusion that none of the phases employed gave unambiguous dependence.

A systematic study of the elution data based on Kovats's indices of some 250 compounds obtained on squalane at four temperatures was published by *Hively* [18]. The work contains elution indices of alkanes, cyclanes, and aromates.

Considering the available elution data contained in the literature squalane seems to be a suitable phase for the analysis of the products of hydroisomerization of C₈-aromates on a capillary column.

Experimental

Capillary column coated with squalane (BDH, Ltd., England) was made using the dynamic method of *Ettre* [21]. The operating conditions are listed in Table 1.

Table 1

Operating conditions

Apparatus	Chrom II
Detector	FID
Column	45 m/0.25 mm
Temperature	49 and 55°C
Carrier gas	Nitrogen
Inlet pressure	1.4 kp/cm ²
Sample	0.7 µl
Splitting ratio	1 : 100

Table 2

Elution data of C₈-isocyclic hydrocarbons on squalane at 49°C

No.	Hydrocarbon	B.p. [°C] [5, 20]	Elution index		Elution time relative to <i>n</i> -hexane	
			Calc.	Ref. [18]	Calc.	Ref. [12]
25	1,1,3-trimethylcyclopentane	104.89	723.9	724.0	3.41	3.4
30	1- <i>trans</i> -2- <i>cis</i> -4-trimethylcyclopentane	109.29	740.7	741.3	3.94	4.0
32	1- <i>trans</i> -2- <i>cis</i> -3-trimethylcyclopentane	110.20	747.8	748.0	4.37	4.3
35	1,1,2-trimethylcyclopentane	113.73	761.0	761.5	5.06	5.1
39	1- <i>cis</i> -2- <i>cis</i> -4-trimethylcyclopentane	115.65	773.3	773.6	5.57	5.6
40	1- <i>cis</i> -2- <i>trans</i> -4-trimethylcyclopentane	116.73	774.8	774.1	5.72	5.7
41	1- <i>cis</i> -2- <i>trans</i> -3-trimethylcyclopentane	117.50	778.7	779.3	5.94	5.9
42	1- <i>trans</i> -4-dimethylcyclohexane	119.35				6.4
	1,1-dimethylcyclohexane (S)	119.54	784.5	—	6.33	6.5
	1- <i>cis</i> -3-dimethylcyclohexane	120.35				6.4
43	1-ethyl- <i>trans</i> -3-methylcyclopentane	120.80	787.8	790.5	6.53	6.7
	1-ethyl- <i>cis</i> -3-methylcyclopentane	121.40				6.4
44	1-ethyl- <i>trans</i> -2-methylcyclopentane	121.20	790.6	791.4	6.70	6.7
45	1-ethyl-1-methylcyclopentane	121.52	794.7	—	6.91	6.9
46	1- <i>cis</i> -2- <i>cis</i> -3-trimethylcyclopentane	123.00	—	—	7.36	7.3
47	1- <i>trans</i> -2-dimethylcyclohexane (S)	123.40	802.2	—	7.47	7.4
48	1- <i>cis</i> -4-dimethylcyclohexane (S)	124.32	805.8	—	7.75	7.7
	1- <i>trans</i> -3-dimethylcyclohexane	124.45				
49	isopropylcyclopentane	126.42	812.7	812.2	8.30	8.3
50	1-ethyl- <i>cis</i> -2-methylcyclopentane	128.05	821.1	821.1	9.03	8.9
51	1- <i>cis</i> -2-dimethylcyclohexane (S)	129.73	829.3	—	9.78	9.8
52	<i>n</i> -propylcyclopentane (S)	130.95	830.7	830.3	9.91	9.8
53	ethylcyclohexane (S)	131.78	835.6	—	10.39	10.3
54	ethylbenzene (S)	136.19	836.5	835.9	10.45	—
55	<i>p</i> -xylene (S)	138.35	849.8	850.0	11.98	—
56	<i>m</i> -xylene (S)	139.10	852.2	852.3	12.27	—
57	<i>o</i> -xylene (S)	144.41	869.9	870.7	14.63	—

(S) — standard hydrocarbon.

Table 3

Elution data of the side-reaction products on squalane at 49°C

No.	Hydrocarbon	B.p. [°C] [5, 20]	Elution index	
			Calc.	Ref. [18]
1	methane, ethane			
2	propane			
3	isobutane			
4	<i>n</i> -butane			
5	isopentane			
6	<i>n</i> -pentane		Identified according to [5, 19]	
7	2,2-dimethylbutane			
8	cyclopentane			
9	2,3-dimethylbutane			
10	2-methylpentane			
11	3-methylpentane			
12	<i>n</i> -hexane (S)	68.74	600.0	600.0
13	methylcyclopentane (S)	71.81	619.1	628.6
14	benzene (S)	80.10	633.3	637.6
15	cyclohexane (S)	80.74	661.5	633.8
16	2-methylhexane	90.05	666.1	666.9
17	1,1-dimethylcyclopentane	87.85	671.3	671.9
18	3-methylhexane	91.85	675.9	676.4
19	1- <i>cis</i> -3-dimethylcyclopentane	90.77	683.0	683.2
20	1- <i>trans</i> -3-dimethylcyclopentane	91.72	687.1	687.5
21	1- <i>trans</i> -2-dimethylcyclopentane	91.87	691.0	689.8
22	<i>n</i> -heptane (S)	98.43	700.0	700.0
23	2,2-dimethylhexane	106.84	719.3	719.7
24	1- <i>cis</i> -2-dimethylcyclopentane	99.53	722.0	721.6
25	methylcyclohexane (S)	100.93	726.5	726.6
27	2,5-dimethylhexane	109.10	728.9	728.5
28	2,4-dimethylhexane	109.43	732.1	732.1
29	ethylcyclopentane	103.47	732.4	734.4
31	toluene (S)	110.62	744.0	746.8
33	2,3,4-trimethylpentane	113.47	752.6	752.5
34	2,3-dimethylhexane	115.61	760.5	760.3
36	2-methylheptane	117.65	765.1	764.8
37	4-methylheptane	117.71	767.4	767.0
38	3-ethylhexane	118.59	772.9	772.4
46	<i>n</i> -octane (S)	125.67	800.0	800.0
58	unidentified	140.50	858.6	—

(S) — standard hydrocarbon.

The individual hydrocarbons in the reaction mixture were identified by comparison with authentic standards (Tables 2 and 3) and the elution data found in the literature [12, 18]. The obtained results were compared also with those of other authors working on the same stationary phase [5, 19]. The Kovats's elution indices obtained with the accuracy of ± 1 index unit from the chromatogram (Fig. 2) under the described working conditions (Table 1) at 49°C are summarized in Tables 2 and 3. Some of the C₇- and C₈-isoalkanes, such as dimethylpentanes, 3-ethylpentane, 3-methylpentane, and methyl-ethylpentanes as well as trimethylpentanes, which might have been in small concen-

tration eluted together with some of the identified hydrocarbons are not contained in Table 3.

When quantitative work was done FID response factors (factor 1) were assumed to be the same for all the compounds under investigation. The boiling points of the individual hydrocarbons are taken from the reference [5, 20].

Results and Discussion

Hydroisomerization of ethylbenzene, ethylcyclohexane, *o*-, *m*-, and *p*-xylene on difunctional catalysts results in the formation of the same hydrocarbons (Tables 2 and 3). Olefinic hydrocarbons were not identified. The number of compounds produced depends on reaction conditions. Under mild conditions (temperature in the range of 300–370°C) hydrocarbons of naphthenic character with the preserved cyclopentane or cyclohexane ring having the total number of carbon atoms equal to 8 were identified in the product (Fig. 1, Table 2). Under the applied chromatographic conditions (Table 1) on the squalane-coated capillary column *cis*-1,3-, *trans*-1,4-, 1,1-dimethylcyclohexanes (peak No. 42), *trans*-1,3-, *cis*-1,4-dimethylcyclohexanes (peak No. 48), *trans*-1,3-, and *cis*-1,3-ethylmethylcyclopentanes (peak No. 43) could not be separated. All of the theoretically possible isomers of trimethylcyclopentane were identified. 1-*cis*-2-*cis*-3-Trimethylcyclopentane was eluted together with *n*-octane.

In addition to hydroisomerization, side reactions (hydrogenolysis, hydrocracking, disproportionation, hydrodealkylation) responsible for the presence of the corresponding hydrocarbons (Table 3, Fig. 2) in the reaction product take place under more drastic reaction conditions. The analysis of the product obtained at 300–370°C showed the presence of a peak between *m*-xylene (56) and *o*-xylene (57). The peak (58) was not present in the product obtained at the temperatures above 400°C under which conditions, however, noticeable amounts of C₉-aromates, eluted after *o*-xylene, were detected. We assume that the peak (58) corresponds to either C₉-alkylcyclohexanes or C₉-alkylcyclopentanes.

Of all the alkanes 3-ethylhexane is the only hydrocarbon to appear in relative highest concentration also at lower temperatures (Fig. 1). The elution pattern of the isomerate obtained at higher temperatures is showed in Fig. 2.

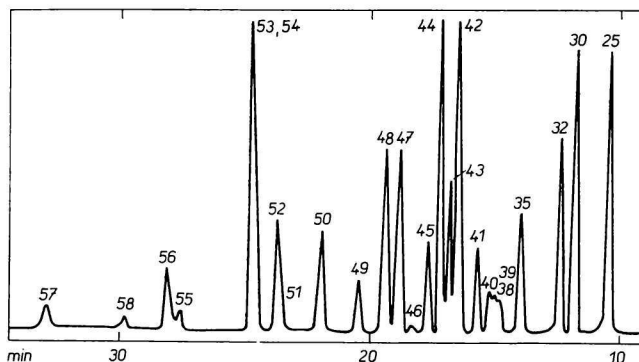


Fig. 1. Separation of isocyclic C₈-hydrocarbons on squalane at 55°C.

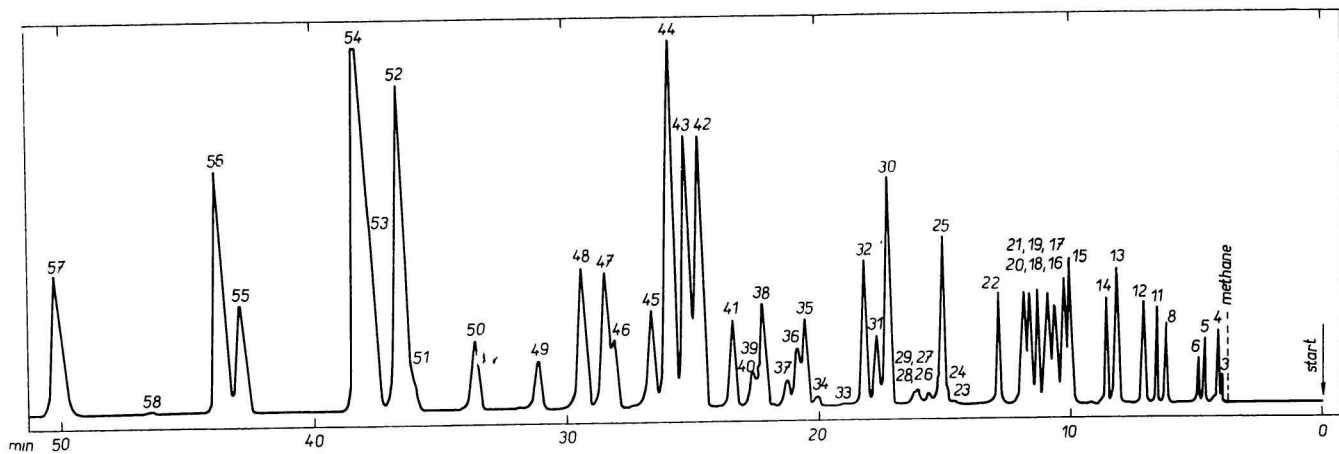


Fig. 2. Separation of the components of the reaction mixture at 49°C.

A linear function has been obtained for the found elution indices plotted against the boiling points of the individual C_6-C_8 components (Fig. 3). The alkanes, cyclanes, and aromates are eluted in groups according to their boiling points. The graph shows evidently the increase of the elution times of the cyclanes and the decrease of the elution times of the aromates relative to the alkanes having the same boiling point. The retar-

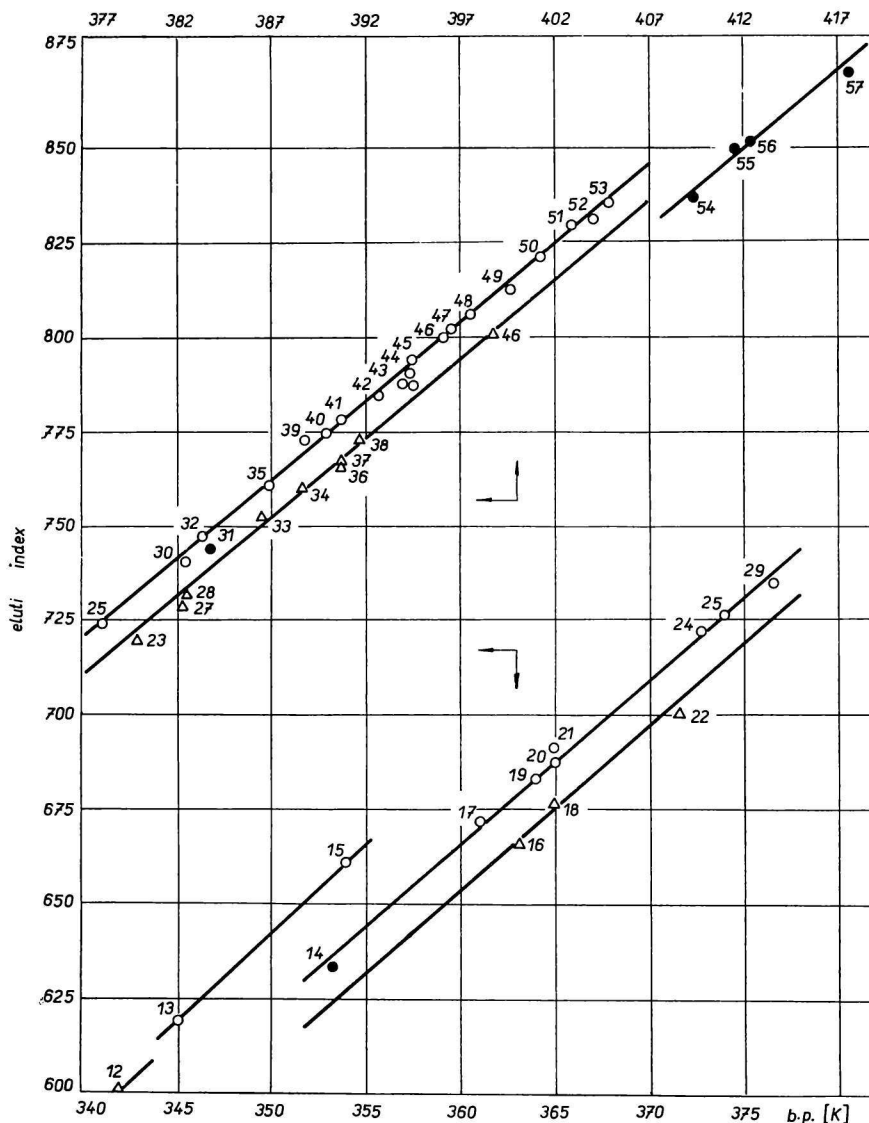


Fig. 3. Dependence of the elution indices upon the boiling points of the hydrocarbons.
○ cyclanes; ● aromates; △ alkanes.

dation in the elution of benzene and toluene makes these two hydrocarbons fit into the linear function of the elution of C_7 - or C_8 -cyclanes. This permits an orientational peak matching for alkanes, cyclanes or aromates in an analyzed mixture of unknown composition. The decrease of elution times of aromatic hydrocarbons relative to the corresponding alkanes has been observed also by Sanders [5].

The decrease and the increase of the elution indices (ΔI) of aromates and cyclanes, respectively, relative to the corresponding alkanes can be numerically expressed by the section on the axis of the elution indices (Fig. 3), since the two lines are parallel; ΔI for the C_8 -cyclanes is equal to 10 and for the C_8 -aromates is equal to 5 index units. The found difference is sufficient for the determination of the elution indices with the accuracy of ± 1 index unit for the characterization of a decrease or increase of the elution times.

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