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Abstract

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CATALYTIC CYCLIZATION OF *n*-PENTANE AND *n*-HEXANE WITH FORMATION OF A FIVE-MEMBERED RING

In a number of works published in recent years, we have shown that paraffin hydrocarbons, in the presence of platinized carbon, are smoothly cyclized into cyclopentane homologs ([1]-[5]). It was found that the yields of cyclopentane hydrocarbons depend substantially on the structure of the initial paraffin hydrocarbons. Thus, at 310° and a space velocity of 0.2 hr^{-1}, the yield of cyclopentane homologs over a fresh catalyst preparation is: from isooctane, 25–35%; from 3-ethylpentane, 12%; and from *n*-octane, 3–5%. One might have thought that paraffins of normal structure are cyclized at approximately the same rate, since *n*-heptane and *n*-octane under somewhat different conditions gave the same yield of cyclization products ([1]). It was therefore of interest to compare *n*-octane with *n*-hexane and *n*-pentane. The latter hydrocarbon was of particular interest, since in the cyclization reaction with formation of a five-membered ring it represents an exception in light of thermodynamic data. Indeed, in a thermodynamically equilibrium mixture of *n*-pentane with cyclopentane at 500° K and atmospheric pressure, cyclopentane should be present in an amount of only 8%, whereas in equilibrium mixtures of *n*-hexane, *n*-heptane, and *n*-octane with the corresponding polymethylenes, the content of cyclopentane hydrocarbons will be 30–40% ([3]).

The investigation carried out by us showed that *n*-pentane indeed behaves differently from all its homologs studied, whereas *n*-hexane is cyclized similarly to *n*-octane. Thus, at 310° and a space velocity of 0.2 hr^{-1}, even over a freshly prepared catalyst, *n*-pentane did not change at all, whereas *n*-hexane was cyclized to the extent of 3.5–4.5%. Moreover, *n*-pentane did not undergo cyclization even at 330°, and only at 350° did it enter into this reaction; but even at this relatively high temperature the yield of cyclopentane was small. Meanwhile, the catalyst was sufficiently active, since over a separate portion of it at 310° and a space velocity of 0.2 hr^{-1} isooctane was cyclized to the extent of 30%.

To confirm that the expected cyclization products were actually obtained in the cases under consideration, the hydrocarbons were passed, each over a separate portion of catalyst, for several days. *n*-Pentane was passed at 350°, *n*-hexane at 310°; the space velocity was the same, namely 0.2 hr^{-1}. The resulting catalyzates, after determination of the constants and chromatography, were distilled on efficient columns. From the *n*-pentane catalyzate, individual cyclopentane was isolated, which, judging from the constants, had a degree of purity of about 99%. From the *n*-hexane catalyzate, a concentrate was isolated which, on the basis of analysis by means of combination-scattering spectra,* contained about 95% methylcyclopentane.

* The combination-scattering spectra of the catalyzates were investigated by Kh. E. Sterin, to whom we express our gratitude for comradely assistance.

It is very curious that in the head fraction from the distillation of the products of the conversion of *n*-pentane, 25–30% isopentane (1.7% based on the whole catalyzate) was detected from the combination-scattering spectra. Until now, reliable evidence for the possibility of isomerization of paraffin hydrocarbons in the presence of platinized charcoal has not been encountered in the literature. It is true that in 1937 Yu. K. Yur' ev and P. Ya. Pavlov ([6]) reported that *n*-octane in a stream of hydrogen is isomerized in the presence of this catalyst into a mixture of isoparaffins, and this work is often mentioned in the monographic literature. However, in the light of our work on the cyclization of paraffins into cyclopentanes, one might think that the isoparaffins in the work of these authors could also have been secondary products: the result of cyclization of *n*-octane and subsequent hydrogenolysis of cyclopentane hydrocarbons, for example:

$$n\text{-}C_8H_{18} \xrightarrow{-H_2} \text{(cyclopentane ring)-}CH_2 - CH_2 - CH_3 \xrightarrow{+H_2} CH_3 - CH(CH_3) - CH_2 - CH_2 - CH_2 - CH_2$$

Since in the hydrogenolysis of cyclopentane only *n*-pentane can be formed, the appearance of isopentane in the catalyzate is evidently due to direct isomerization.

Experimental Part

Starting substances and catalysts. *n*-Pentane and *n*-hexane were obtained by chromatographing commercial preparations of these hydrocarbons and then distilling them on a column with an efficiency of 1000 theoretical plates. After distillation they had the following constants:

	b.p., °C (760 mm)	n_D^{20}	d_4^{20}
n-Pentane	36.1	1.3575	0.6262
n-Hexane	69.0	1.3749	0.6594

These values practically coincide with the most reliable literature data ([7]).

Two samples of platinized charcoal (20% Pt), prepared according to the prescription of N. D. Zelinskii and M. B. Turova-Polyak ([8]), served as the catalyst.

To compare the activity of the catalysts with samples used previously, small portions of the catalysts (10 ml) were tested with isooctane at 310° and a space velocity of 0.2 hr^{-1}. After chromatography the catalyzates had n_D^{20} 1.3975 and 1.3962, which corresponds to 30 and 24% yields of 1,1,3-trimethylcyclopentane, respectively. On the first of the samples the cyclization of *n*-pentane was studied; on the second, *n*-hexane was cyclized.

Cyclization of *n*-pentane. Over 60 ml of catalyst, 6 experiments of 2–4.5 hr duration were carried out. Each time a fresh portion of *n*-pentane was passed at 350° and a space velocity of 0.2 hr^{-1}, without a carrier gas. For each catalyzate the refractive index, specific gravity, and bromine number were determined. Then, by passage through silica gel, the catalyzates were freed of unsaturated compounds, after which the refractive index and specific gravity were again determined. The content of unsaturated compounds was found from the bromine numbers, and that of cyclopentane on the basis of the additivity of refractive indices and specific volumes ([9]), as the mean of these two values. The results of the investigation of the catalyzates before and after chromatography are given in Table 1.

The chromatographed catalyzates from all experiments were combined. As a result, 107.0 g of catalyzate with n_D^{20} 1.3593 was obtained, which approximately corresponds to a cyclopentane content of 3.7%. The catalyzate was distilled on a column with an efficiency of 100 theoretical plates, and the residue from this distillation was then further distilled on a column with an efficiency of 35 theoretical plates. Summary results of the distillation are given in Table 2. In the investigation of fraction I by means of combination-···

Table 1

Yields and properties of *n*-pentane catalysts

Experiment no.	*n*-Pentane passed, g	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties after chromatography	Catalyst properties after chromatography	Catalyst properties after chromatography
		yield, g	n_D^{20}	d_4^{20}	bromine number	unsaturates content, %	n_D^{20}	d_4^{20}	cyclopentane content*, %
1	28.8	28.0	1.3612	0.6328	7.3	3.3	1.3593	0.6312	4.2
2	29.4	27.0	1.3605	0.6325	9.9	4.4	1.3592	0.6314	4.2
3	31.3	30.0	1.3602	0.6307	9.0	4.0	1.3592	0.6303	3.7

Experiment no.	n-Pentane passed, g	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties before chromatography	Catalyst properties after chromatography	Catalyst properties after chromatography	Catalyst properties after chromatography
4	12.5	11.3	1.3604	0.6313	8.0	3.6	1.3590	0.6301	3.3
5	24.1	23.8	1.3603	0.6315	9.3	4.1	1.3592	0.6311	4.1
6	27.5	26.5	1.3600	0.6302	9.5	4.2	1.3590	0.6294	3.0

* Calculated as the average from the values found from refractive indices and specific volumes.

Table 2

Results of distillation of the n-pentane catalyst*

Fraction no.	Boiling limits, °C (at 760 mm Hg)	Fraction yields, %	n_D^{20}	d_4^{20}	Cyclopentane content, %
I	29.5—36.1	3.9	1.3560	0.6235	—
II	36.1	4.7	1.3575	0.6262	—
III	36.1	77.9	1.3575	0.6262	—
IV	36.1	2.3	1.3575	0.6262	—
V	36.1	0.9	1.3575	0.6262	—
VI	36.1—49.2	1.4	1.3915	0.7071	69
VII**	49.2	2.9	1.4063	0.7438	99
Residue	—	0.3	1.4063	—	99
Collected in trap	—	2.3	1.3565	0.6248	—
Losses	—	3.4			
Total···		100.0			

* Fractions I—IV were collected on a column with an efficiency of 100 theoretical plates; the remaining fractions, on a column with an efficiency of 35 theoretical plates.
** The aniline point of this fraction is 16.0°.

By selective scattering, all the principal lines of isopentane were detected, its content being 25—30%, which amounts to 1.7% in the catalyst. A calculation made on the assumption of additivity of the refractive indices of isopentane and *n*-pentane led to a close value (2.1%).

The constants of fraction VII of this distillation are very close to the constants of cyclopentane. According to the most reliable literature data this hydrocarbon has the following properties: b.p. 49.262°/760 mm; n_D^{20} 1.40645; d_4^{20} 0.74538 (7); aniline point 15.8° (9). Still closer to the constants of fraction VII are the constants calculated for a mixture of 99% cyclopentane and 1% *n*-pentane: n_D^{20} 1.4061; d_4^{20} 0.7440 and aniline point 16.3°.

C y c l i z a t i o n o f *n*-h e x a n e. Over 45 ml of catalyst, 9 runs of 5 hr each were carried out. Each time a fresh portion of *n*-hexane was passed at 310° and a space velocity of 0.2 hr^{-1} without a carrier gas. All subsequent treatment of the catalysts and determination of the content of olefins and cyclanes in them was carried out in the same way as in the case of *n*-pentane. The benzene content in the catalyst was calculated from the change in refractive index before and after chromatography. The results obtained are summarized in Table 3.

Table 3

Yields and properties of the catalysts of *n*-hexane

Experiment No.	*n*-Hexane passed, g	Yield, %	n_D^{20} before chromatography	d_4^{20} before chromatography	Bromine number before chromatography	n_D^{20} after chromatography	d_4^{20} after chromatography	Olefins, %	Benzene, %	Methylcyclopentane, %	*n*-Hexane, %
1	29.4	91.4	1.3774	0.6648	0.9	1.3765	0.6627	0.5	1.0	4.5	94.0
2	28.9	93.4	1.3774	0.6648	1.3	1.3763	0.6623	0.7	1.3	4.0	94.0
3	30.3	93.1	1.3772	0.6637	1.2	1.3761	0.6619	0.6	1.0	3.4	95.0
4	28.6	93.3	1.3770	0.6635	1.0	1.3760	0.6615	0.5	1.1	3.0	95.4
5	27.2	96.6	1.3768	0.6631	1.2	1.3759	0.6613	0.6	1.0	2.9	95.5
6	30.1	93.3	1.3768	0.6630	1.2	1.3758	0.6608	0.6	1.1	2.2	96.1
7	29.7	99.6	1.3768	0.6630	1.3	1.3758	0.6609	0.7	1.0	2.5	95.8
8	28.9	93.4	1.3767	0.6628	1.4	1.3756	0.6608	0.8	1.1	1.9	96.2
9	29.4	90.0	1.3767	0.6628	1.3	1.3756	0.6608	0.7	1.1	1.9	96.3

Distillation on a column of the combined chromatographed catalyst (185.3 g) with n_D^{20} 1.3760 (3.1% methylcyclopentane) was carried out with reflux ratios of 240 in the sections of temperature rise and 100 on the plateau. The results are presented in Table 4. As the constants show, methylcyclopentane

Table 4

Results of distillation of the *n*-hexane catalyst

Fraction No.	Boiling limits, °C (760 mm Hg)	Fraction yields, %	n_D^{20}	d_4^{20}
I	56.6–67.6	1.0	1.3760	0.6614
II	67.6–68.9	1.5	1.3748	–
III	68.9–69.2	86.1	1.3749	–
IV	69.2	0.7	1.3754	–
Residue	–	2.6	–	–
Losses	–	8.1	–	–

became concentrated in the residue, containing, according to refractive index, 94.7%, and according to specific volume 96.1%, of this hydrocarbon. Analysis of the residue by means of combination-scattering spectra also showed that it consists of 95% methylcyclopentane and 5% *n*-hexane.

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CITED LITERATURE

1. B. A. Kazanskii, A. L. Liberman et al., DAN, **95**, 77 (1954).
2. B. A. Kazanskii, A. L. Liberman, V. T. Aleksanyan, Kh. E. Sterin, DAN, **95**, 281 (1954).
3. A. L. Liberman, T. V. Lapshina, B. A. Kazanskii, DAN, **105**, 727 (1955).
4. A. L. Liberman, T. V. Vasina, B. A. Kazanskii, DAN, **117**, 430 (1957).
5. B. A. Kazanskii, A. L. Liberman, M. Yu. Lukina, I. V. Gostunskaya, Khim. nauka i promyshl., **2**, 172 (1957).
6. Yu. K. Yur' ev, P. Ya. Pavlov, ZhOKh, **7**, 97 (1937).
7. D. Rossini et al., *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Pittsburgh, 1953.
8. N. D. Zelinskii, M. B. Turova-Polyak, *Selected Works of Academician N. D. Zelinskii*, **2**, Publishing House of the Academy of Sciences of the USSR, 1941, pp. 150, 224.

9. B. A. Kazanskii, T. F. Bulanova, Izv. AN SSSR, OKhN, **1947**, 29.

Note: Figure translations are in progress. See original paper for figures.