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1961

SovietRxiv

Abstract

Full Text

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CONTACT TRANSFORMATIONS OF CYCLOOCTANE IN THE PRESENCE OF A NICKEL CATALYST

In 1908 Willstätter and Kametaka ([1]) attempted to study the transformations of cycloheptane and cyclooctane over nickel at 205—250°. Work with small quantities of substances (2-3 g) and the lack of refined methods of investigation did not allow the authors to identify the reaction products. However, they suggested that, as a result of passing cycloheptane vapors over nickel in a stream of hydrogen at 235°, methylcyclohexane is formed, and at 250°, aromatic hydrocarbons. Cyclooctane, in their opinion, isomerizes at 205—210° mainly to dimethylcyclohexane, possibly with an admixture of alkylated cyclopentanes. The authors specifically noted that paraffins of normal structure, namely, *n*-heptane and *n*-octane, were not detected.

In the present work, the transformations of cyclooctane over a nickel catalyst (50% nickel on kieselguhr) at 200 and 250° in a stream of hydrogen were investigated. The catalyzate obtained from cyclooctane at 200° was passed twice more in succession over the catalyst at the same temperature. The conversion of cyclooctane was ~ 61%, while double contact treatment at 250° caused conversion of cyclooctane by ~ 81%. The resulting final catalyzates were distilled on an efficient column, and the composition of the fractions was investigated by means of combination-scattering spectra. As a result of the determinations carried out, the following composition of the catalyzates was established: the catalyzate obtained at 200° consisted of *n*-octane (~ 15% of the weight of the liquid part of the catalyzate), cycloheptane (~ 6%), cis-1,2-dimethylcyclopentane (~ 5%), *n*-heptane (~ 4%), methylcyclohexane (~ 3%), cyclohexane (less than 1%), and a very small amount of cis-bicyclo-(0,3,3)-octane-(cis-pentalane). In addition, there are grounds to suppose the presence in the catalyzate of trans-1,2-dimethylcyclohexane. About 46.5% of the weight of the catalyzate is accounted for by unreacted cyclooctane. The data obtained make it possible to propose the following reaction scheme:

The catalyst obtained at 250° consisted, in addition to unreacted cyclooctane, of *cis*-pentalane (~8% of the catalyst weight), toluene (~11%), and benzene (~2%). In addition, the following were detected: methylcyclohexane, cyclohexane, *cis*-1,2-dimethylcyclopentane, and gem-dimethylcyclohexane, whose quantitative ratios could not be determined. The data obtained make it possible to propose the following scheme for the transformations of cyclooctane over a nickel catalyst at 250°:

reaction scheme: cyclooctane transforms to n-C_8H_{18}, then to n-C_7H_{16}; also to methylcycloheptane, cycloheptane, methylcyclohexane, cyclohexane, dimethylcyclopentane, and bicyclic products

Figure 1: reaction scheme: cyclooctane transforms to n-C_8H_{18}, then to n-C_7H_{16}; also to methylcycloheptane, cycloheptane, methylcyclohexane, cyclohexane, dimethylcyclopentane, and bicyclic products

reaction scheme

Figure 2: reaction scheme

Thus, when cyclooctane is passed over nickel deposited on kieselguhr, in a strong stream of hydrogen under comparatively mild temperature conditions (200–250°), three processes take place: hydrogenolysis of the eight-membered ring, observed by us for the first time, with formation of n-octane, analogous to the hydrogenolysis of compounds with smaller rings ([2]–[5]); transannular dehydrogenation, leading to *cis*-pentalane; and stepwise isomerization of cyclooctane into compounds with seven-, six-, and five-membered rings. In the quantitative ratio of these processes, the reaction temperature plays a considerable role. Thus, hydrogenolysis of cyclooctane proceeds to an appreciable extent only at 200°, while at 250° this process is practically not observed; by contrast, formation of pentalane is characteristic mainly of 250°. The processes of ring isomerization, accompanied by hydrocracking, occur both at 200° and at 250°; however, at 250° they are, in addition, further complicated by aromatization of hexamethylene hydrocarbons. It is interesting to note that the *cis*-1,2-dimethylcyclopentane detected in the catalysts is probably formed as a result of the indicated isomerization processes. This is confirmed by the fact that the catalyst obtained at 200° contains more of this hydrocarbon than the catalyst

Table 1

Fraction No.	Boiling range at 727 mm, °C	n_D^{20}	d_4^{20}	Anil. point	Amount, g	Amount, wt. %
1	up to 93.7	1.3885	–	–	0.95	4.4
2	93.7-103	1.3970	0.7070	–	1.66	7.7
3	103-119	1.4211	0.7604	–	1.4	6.5
4	119-130	1.4095	0.7337	59.8	4.57	21.2

Fraction No.	Boiling range at 727 mm, °C	n_D^{20}	d_4^{20}	Anil. point	Amount, g	Amount, wt. %
5	130-140	1.4431	0.8150	–	2.56	11.9
6	140-149	1.4581	0.8372	–	5.83	27.0
7	Residue	1.4587	0.8348	–	4.14	19.2
	Losses	–	–	–	0.45	2.0

Table 2

Hydrocarbons included in the fractions	1+2	3	4	5	6	7	Total in the catalyzate, g	Total in the catalyzate, wt. %
n-Heptane	30	–	–	–	–	–	0.8	3.7
n-Octane	–	15	60	+*	–	–	3.1	14.5
cis-1,2-Dimethylcyclopentane	40	–	–	–	–	–	1.0	4.6
Cyclohexane	5	–	–	–	–	–	0.13	0.6
Methylcyclohexane	15	–	–	–	–	–	0.6	2.8
Cycloheptane	–	35	15*	–	–	–	1.2	5.5
cis-Pentalane	–	–	+	–	–	–		
Cyclooctane	–	–	–	–	Main content		10	46.5

* Hydrocarbon detected qualitatively.

obtained at 250°, whereas in the case of formation of cis-1,2-dimethylcyclopentane from cis-pentalane, as a result of the hydrogenolysis of cis-pentalane and the hydrocracking of the 1-methyl-2-ethylcyclopentane thereby formed, there should have been more cis-1,2-dimethylcyclopentane at 250°, since at 200° cis-pentalane is scarcely formed, and 1-methyl-2-ethylcyclopentane was not found in the

catalyzate at all. The decrease in the amount of cis-1,2-dimethylcyclopentane when the reaction is carried out at 250° can be explained by the fact that, in this case, competing processes occur: formation of cis-1,2-dimethylcyclopentane from methylcyclohexane, on the one hand, and of aromatic hydrocarbons (benzene and toluene), on the other, and the equilibrium is shifted toward the formation of the latter. At 200° aromatization processes do not occur, and therefore at this temperature the percentage conversion of methylcyclohexane to cis-1,2-dimethylcyclopentane is greater than at 250°.

It should also be noted that transannular dehydrogenation of cyclooctane to cis-pentalane and isomerization of hydrocarbons also proceed in the presence of platinized charcoal, but at a higher temperature, namely at 310° (6,7). Experiments specially carried out by us showed that cyclooctane passed over active 5% platinized charcoal in a stream of hydrogen at temperatures of 200 and 250° is unchanged.

Experimental part

The cyclooctane (7) used in the work had the following constants: b.p. 149.5° (745 mm); n_D^{20} 1.4588; d_4^{20} 0.8356. Literature data (8): b.p. 150.7° (760 mm); n_D^{20} 1.45837; d_4^{20} 0.8362.

Contact transformations of cyclooctane at 200°. In a quartz tube were placed 48 ml (41.2 g) of a nickel catalyst consisting of equal amounts of nickel and kieselguhr; over it, in a strong stream of hydrogen at 200°, 26 g of cyclooctane was passed at a space velocity of 0.28. The resulting catalyzate was subjected twice more to contacting under the same conditions; the following results were obtained:

	Run No. 1	Run No. 2	Run No. 3
Amount of catalyzate, g	24.1	22.3	21.56
n_D^{20}	1.4470	1.4370	1.4350

The total losses, including the formation of gaseous hydrocarbons, after threefold contacting amounted to ~16%.

The catalyzate, which showed a negative formalite reaction (indicating the absence of aromatic and unsaturated hydrocarbons), was fractionated on a 40 theoretical-plate column. The results of the distillation are presented in Table 1.

The composition of all fractions was established by studying their Raman spectra (see Table 2).

The presence in the spectra of the third and fourth fractions of lines at 500 cm^{-1} and 749 cm^{-1} gives grounds for assuming the presence in these fractions of trans-1,2-dimethylcyclohexane. In addition, on examining the fifth fraction, bright

lines at 730 cm^{-1} and 1002 cm^{-1} were found in its spectrum, which could not be identified.

Contact transformations of cyclooctane at 250°. The experiments were carried out under conditions analogous to those described above. For catalysis, 18.4 g of cyclooctane was taken.

Table 3

Fraction Nos.	Boiling limits at 745 mm, °C	n_D^{20}	d_4^{20}	Amount, g	Amount, wt. %
1	up to 94	1.4110	0.7319	1.18	9.9
2	94–100	1.4010	0.7131	1.33	11.0
3	100–119	1.4585	0.8115	2.20	19.0
4	119–127	1.4112	0.7329	2.90	24.1
5	Residue	1.4594	0.8276	3.40	28.3
	Losses	–	–	0.99	8.3

The catalyzate was again passed over the catalyst; the results of the experiments were as follows:

Passes	No. 1	No. 2
Amount of catalyzate, g	13.4	12.0
n_D^{20}	1.4360	1.4320

The total losses, including the formation of gaseous hydrocarbons, amounted to $\sim 34\%$.

The catalyzate was fractionated on a 40 theoretical-plate column. The results of the distillation are given in Table 3. The composition of all fractions was established by studying their Raman spectra, the results of which are given in Table 4.

Table 4

Hydrocarbons included in the composition of the fractions	Fractions Nos. 1+2	Fractions Nos. 3	Fractions Nos. 4	Fractions Nos. 5	Total in catalyzate, g	Total in catalyzate, wt. %
Hydrocarbons included in the composition of the fractions	Hydrocarbon content, wt. %	Hydrocarbon content, wt. %	Hydrocarbon content, wt. %	Hydrocarbon content, wt. %	Total in catalyzate, g	Total in catalyzate, wt. %
Benzene	10	–	–	–	0.25	7.1
Toluene	+*	60	–	–	1.3	10.8
Cyclohexane	+*	2	–	–		
Methylcyclohexane	+*	3	–	–		
1,1-Dimethylcyclohexane	–	–	2	–	0.06	0.5
cis-1,2-Dimethylcyclopentane	+*	7	–	–	0.2	1.7
trans-1-Methyl-2-ethylcyclopentane	–	–	+*	–		
n-Octane	–	–	+*	+*		
cis-Pentalane	–	–	35	+*	1.0	8.3
Cyclooctane	–	–	–	Principal content	3.4	28.3

* The hydrocarbon was detected qualitatively.

The method of obtaining and measuring the Raman spectra used in the present work is analogous to that described earlier (7).

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Received
11 XI 1960

CITED LITERATURE

1. R. Willstätter, T. Kametaka, *Ber.*, **41**, 1480 (1908).
2. R. Willstätter, J. Bruce, *Ber.*, **40**, 3979 (1907).
3. E. Corner, P. Pease, *Ind. and Eng. Chem. Anal. Edition.*, **12**, 564 (1945).
4. B. A. Kazanskii, S. R. Sergienko, *ZhOKh*, **9**, 447 (1939).
5. B. A. Kazanskii, Z. A. Rumyantseva, *Izv. AN SSSR, OKhN*, 1947, 183.
6. S. I. Khromov, E. S. Balenkova, B. A. Kazanskii, *Vestn. MGU*, No. 2, 36 (1960).
7. B. A. Kazanskii, E. A. Shokova, S. I. Khromov, V. T. Aleksanyan, Kh. E. Sterin, *DAN*, **133**, No. 5, 1090 (1960).
8. S. Kaarsemaker, J. Coops, *Rec. trav. chem., Pays-Bas*, **71**, 261 (1952).

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