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Abstract

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DEHYDROGENATION OF FIVE-MEMBERED CYCLENES IN THE PRESENCE OF ACTIVATED CARBON

The catalytic properties of wood charcoal, in particular birch activated carbon, have so far been studied insufficiently. However, a number of works have made interesting observations concerning the ability of wood charcoal to carry out various reactions. Thus, Barr ([1]), and subsequently Balandin and co-workers ([2]), established the catalytic action of activated carbon in the dehydration of cyclohexanol. P. G. Ivanov showed that highly active birch charcoal is capable, at 350°, of carrying out the dehalogenation reaction of chloro-, bromo-, and iodobenzene in a hydrogen atmosphere ([3]), and at 300° of activating the halogenation reaction of benzene ([4]). Moldavskii and co-workers ([5]) found that active wood charcoal can also carry out the dehydrogenation reaction of cyclohexane at 530–560° with a low space velocity of about 0.14 hr^{-1}. From the transformations of certain terpenes ([6]) and cyclohexene ([7]), the ability of activated carbon to carry out irreversible catalysis was established. Kazanskii and co-workers ([8]) showed that activated carbon can carry out the isomerization reaction of alkylcyclopropanes and the hydrogenation of the alkenes formed in this process. In addition, carbon proved to be an effective dealkylating catalyst ([9]) in the demethylation reaction of toluene to benzene.

The present investigation was undertaken in order to study the behavior of five-membered cyclenes under the action of various activated carbons at elevated temperatures and reduced pressure.

We have established that in the presence of wood activated carbon from the Perm plant, fine-grained BAU carbon, and also bone char, at 600° and at a pressure reduced to 10–15 mm, cyclopentene, as well as methylcyclopentene, undergo dehydrogenation to cyclopentadiene and methylcyclopentadiene; the degree of conversion reaches 5 and 48%, respectively:

$$\text{cyclopentene with substituent } (R) \longrightarrow \text{cyclopentadiene with substituent } (R) + H_2, \quad \text{where } R = H \text{ or } CH_3.$$

Meanwhile, methylcyclopentene passed under the same conditions over crushed quartz underwent no noticeable changes.

In the catalyzates of 1-methylcyclopentene-1, in addition to methylcyclopentadiene, about 5% cyclopentadiene, 5% 1-methylcyclopentene-2, and up to 10% benzene, calculated on the initial cyclene, were detected. One of the possible pathways for the formation of benzene is apparently the isomerization of methylcyclopentene to cyclohexene with its subsequent dehydrogenation:

$$\text{1-methylcyclopentene} \longrightarrow \text{cyclohexene} \longrightarrow \text{benzene} + 2H_2.$$

2-Methylcyclopentene-1 was evidently formed as a result of migration of the double bond in the initial hydrocarbon:

$$\text{methylcyclopentadiene structure with CH}_3 \longrightarrow \text{isomeric methylcyclopentadiene structure with CH}_3$$

whereas cyclopentadiene is, in all probability, either the product of hydrogenolysis of the methyl group of the methylcyclopentadiene formed:

$$\text{methylcyclopentadiene structure with CH}_3 + \text{H}_2 \longrightarrow \text{cyclopentadiene} + \text{CH}_4,$$

or of the initial 1-methylcyclopentene-1, followed by dehydrogenation of cyclopentene:

$$\text{1-methylcyclopentene-1} + \text{H}_2 \xrightarrow{-\text{CH}_4} \text{cyclopentene} \longrightarrow \text{cyclopentadiene} + \text{H}_2.$$

The results obtained show that, under the conditions adopted by us, activated carbon possesses high activity for carrying out the reaction of dehydrogenation of five-membered cyclenes to the corresponding cyclopentadiene hydrocarbons, and also, to a much lesser extent, the reactions of dehydroisomerization and dealkylation.

Experimental Part

1-Methylcyclopentene-1 (b.p. 75.5–76°/756, n_D^{20} 1.4330; d_4^{20} 0.7799) was obtained by dehydration of cyclohexanol in contact with aluminum oxide, proceeding with simultaneous ring contraction:

$$\text{cyclohexanol} \xrightarrow[450^\circ]{\text{Al}_2\text{O}_3} \text{1-methylcyclopentene} + \text{H}_2\text{O}.$$

Cyclopentene (b.p. 44.5°/757; n_D^{20} 1.4220; d_4^{20} 0.7714) was synthesized from cyclopentanone according to the scheme:

$$\text{cyclopentanone} \xrightarrow[170^\circ,\ \mathrm{H_2},\ 120\ \text{atm}]{\text{skeletal Ni–Al}} \text{cyclopentanol} \xrightarrow[310^\circ]{\mathrm{MgSO_4}} \text{cyclopentene} + \mathrm{H_2O}.$$

As catalyst, carbon of three grades was taken: wood activated carbon from the Perm plant, with grain size 5—6 mm and ash content 0.48%, fine-grained BAU, and bone charcoal. The samples of activated carbon were preliminarily treated with 10% hydrochloric acid, distilled water, then with a 5% NaOH solution and again with water.

The cyclenes were brought into contact with the carbon in a quartz tube at 450—600° at a rate of 0.25—1.0 hr^{-1}, in portions of 10 ml. The pressure in the reaction zone was maintained within 10—15 mm. In the catalysts obtained, immediately after completion of the experiment, the content of cyclopentadiene or methylcyclopentadiene was determined by Afanas' ev' s method ([10]). The catalysts were then subjected to careful fractionation, and the isolated fractions were analyzed by means of Raman spectra*. The composition of the gaseous products was determined by a chromatographic method ([11]).

* The Raman spectra of the catalysts were investigated by Yu. P. Egorov and G. K. Gaivaronskaya, to whom we express our gratitude.

Table 1

Dehydrogenation of five-membered cyclenes on samples of activated carbon

Catalyst	Starting hydrocarbon	Temp., °C	Space velocity, h^{-1}	Catalyst yield, wt. %	n_D^{20} of the catalyzate	Yield of cyclopentadiene hydrocarbons, % on catalyst	Yield of cyclopentadiene hydrocarbons, % on hydrocarbon passed
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	450	1.0	95.5	1.4357	5	4.8
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	500	1.0	94.8	0.4435	20	19
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	550	1.0	93.3	1.4485	37	34

Catalyst	Starting hydrocarbon	Temp., °C	Space velocity, h^{-1}	Catalyst yield, wt. %	n_D^{20} of the catalyzate	Yield of cyclopentadiene hydrocarbons, % on catalyst	Yield of cyclopentadiene hydrocarbons, % on hydrocarbon passed
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	600	1.0	92.1	1.4520	51	47
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	600	0.75	92.0	1.4515	52	48
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	600	0.5	90.2	1.4525	54	48

Catalyst	Starting hydrocarbon	Temp., °C	Space velocity, h^{-1}	Catalyst yield, wt. %	n_D^{20} of the catalyzate	Yield of cyclopentadiene hydrocarbons, % on catalyst	Yield of cyclopentadiene hydrocarbons, % on hydrocarbon passed
Birch activated carbon from the Perm plant	1-Methylcyclopentene-1	600	0.25	90.9	1.4520	53	48
Fine-grained BAU carbon	Same	600	0.3	83.5	1.4550	49	41
Fine-grained BAU carbon	Same	550	0.3	87.2	1.4435	38	33
Bone charcoal	Same	600	0.3	90.2	1.4500	50	45
Crushed quartz	Same	600	0.3	98.3	1.4330	0.03	Traces
Pumice	Same	600	0.3	98.0	1.4330	0.05	Traces
Birch carbon from the Perm plant	Cyclopentene	600	0.3	88.1	1.4360	60	53

Fig. 1. Change in the activity of carbon with time in experiments at rates: 1 –0.25 h^-1, 2 –0.5 h^-1, 3 –0.75 h^-1, 4 –1.0 h^-1. (Abscissa axis –time in minutes)

Figure 1: Fig. 1. Change in the activity of carbon with time in experiments at rates: 1 –0.25 h^-1, 2 –0.5 h^-1, 3 –0.75 h^-1, 4 –1.0 h^-1. (Abscissa axis –time in minutes)

Catalyst	Starting hydrocarbon	Temp., °C	Space velocity, h^{-1}	Catalyst yield, wt. %	n_D^{20} of the catalyzate	Yield of cyclopentadiene hydrocarbons, % on catalyst	Yield of cyclopentadiene hydrocarbons, % on hydrocarbon passed
Birch carbon from the Perm plant	Cyclopentene	550	0.3	91.3	1.4300	40	36

The results of experiments on the dehydrogenation of cyclopentene and 1-methylcyclopentene-1 are presented in Table 1. As can be seen from the data in Table 1, wood charcoal, as well as bone charcoal, under reduced pressure, have the ability to carry out the dehydrogenation reaction of five-membered cyclenes into the corresponding cyclopentadiene hydrocarbons. At 600° the depth of conversion into the latter is 53-48%, calculated on the starting cyclene passed through. With decreasing temperature the conversion of cyclenes into cyclodienes falls noticeably. Thus, when the temperature is decreased from 600 to 500° at a space velocity of 1.0 h^{-1}, the yield of methylcyclopentadiene in the dehydrogenation reaction of methylcyclopentene decreases from 47 to 19%. At 600° variation of the feed rate of methylcyclopentene to the contact within the limits 0.25-1.0 h^{-1} has no substantial effect on the yield of methylcyclopentadiene. Methylcyclopentene, passed under the same conditions over crushed quartz or pumice, left the reaction zone unchanged; in this case about 2% of the substance was lost to gas formation.

Fig. 1. Change in the activity of carbon with time in experiments at rates: 1 –0.25 h^{-1}, 2 –0.5 h^{-1}, 3 –0.75 h^{-1}, 4 –1.0 h^{-1}. (Abscissa axis –time in minutes)

To determine the catalytic stability of wood charcoal, four series of experiments were carried out in which methylcyclopentene was subjected to dehydrogenation at 600° and a pressure of 15 mm, with space velocities from 0.25 h^{-1} to 1.0 h^{-1}. The results obtained are presented in Fig. 1.

As can be seen from the character of the curves in Fig. 1, the dehydrogenating activity of the carbon gradually decreased with time; moreover, in experiments with a higher feed rate of the starting hydrocarbon it decreased more rapidly. Thus, when methylcyclopentene was passed at a rate of 0.25 h^{-1}, after two hours the degree of its conversion into methylcyclopentadiene was 22%, whereas at a passing rate of 1.0 h^{-1} over the same period of time the yield of methylcyclopentadiene decreased to 9%. Apparently, one of the reasons for the decrease in the dehydrogenating activity of the carbon is the deposition of resinous substances on it. This supposition is consistent with the fact that the specific

the surface of the carbon, determined by the dynamic method (12) from the adsorption of benzene vapor at 20°, decreased from 519 m^2/g to 390 m^2/g after the experiments had been carried out.

In order to determine the composition of the reaction products, 30.5 g of the combined catalyzate obtained in the experiments on the dehydrogenation of 1-methylcyclopentene-1 at 600° was separated on a rectification column with an efficiency of 40 theoretical plates into fractions, which were then subjected to spectral analysis.

Fraction I, with boiling range 47—71°/750 mm, n_D^{20} 1.4240 and d_4^{20} 0.7685, comprising 9.6% of the catalyzate taken for distillation, consisted chiefly of cyclopentadiene (∼ 40%) and 2-methylcyclopentene-1 (∼ 40%), as well as unchanged 1-methylcyclopentene-1 (∼ 20%).

Fraction II, with b.p. 71—77°, n_D^{20} 1.4530; d_4^{20} 0.7945 (67.7%), contained a considerable amount of methylcyclopentadiene together with unchanged 1-methylcyclopentene-1 and benzene (∼ 15%). The residue, amounting to 16.2%, was a thick syrup-like mass, rapidly solidifying on cooling in air, with the composition C 88.3%; H 9.2%. This residue, for the most part, was probably a polymer of methylcyclopentadiene. In the gaseous products from the experiments with methylcyclopentene carried out at 600°, in addition to hydrogen (68.3%), methane (2.0%), ethane (2.5%), ethylene (10.2%), propane (5.1%), and propylene (11.9%) were detected.

The absence of cyclopentane and methylcyclopentane in the catalyzates indicates that, under the selected conditions, the hydrogen redistribution reaction does not occur.

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