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Abstract

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DEHYDROGENATION OF FIVE- AND SIX-MEMBERED CYCLANES IN THE PRESENCE OF ACTIVATED CARBON

It is known from a number of studies that activated carbon possesses catalytic activity in carrying out various reactions. Thus, observations have been made that, under the action of activated carbon, reactions proceed involving the dehydrogenation of terpenes (^{1}) and the dehydration of cyclohexanol (^{2}), the irreversible catalysis of cyclohexene (^{3}) and terpenes (^{1}), the isomerization of alkylcyclopropanes (^{4}) with subsequent hydrogenation of the alkenes formed in this process, the dehalogenation of chloro-, bromo-, and iodobenzene (^{5}), the dehydrogenation of alkyldihydrofurans (^{6}), and other reactions. Recently we showed (^{7}) that under the action of active carbons of various grades—birch carbon from the Perm plant with grain sizes of 5-6 mm, fine-grained "BAU," and bone charcoal—five-membered cyclenes are dehydrogenated under reduced pressure at 500-600° with formation of the corresponding cyclopentadiene hydrocarbons.

There is no information in the literature concerning the possibility of dehydrogenating five-membered cyclanes under the action of activated carbon. As for the behavior of six-membered cyclanes, Moldavskii et al. (^{8}) showed that cyclohexane, passed at 533° with a space velocity of 0.14 hr^{-1} in contact with birch activated carbon, gave benzene in a yield of 17%, and at 560°—56.4%.

In this connection, and also on the basis of our previous observations, we decided to investigate in more detail the catalytic properties of wood activated carbon in the dehydrogenation reaction of five- and six-membered rings.

We have established that five- and six-membered cyclanes, as a result of the catalytic action of wood charcoal, undergo dehydrogenation with a high degree of conversion into the corresponding products. Thus, at 600° under ordinary pressure, the extent of conversion of cyclohexane and methylcyclohexane into benzene and toluene reaches 97 and 100%, respectively. Cyclopentane and methylcyclopentane at the same temperature, but under pressure reduced to 10-15 mm, are converted into the corresponding cyclopentadiene hydrocarbons in yields of 18 and 29%, respectively:

$$\overset{(R)}{\text{cyclohexane ring}} \xrightarrow[600^\circ,\ p=750\ \text{mm}]{\text{activated carbon}} \overset{(R)}{\text{benzene ring}}\ ; \qquad \overset{(R)}{\text{cyclopentane ring}} \xrightarrow[600^\circ,\ p=10\ \text{mm}]{\text{activated carbon}} \overset{(R)}{\text{cyclopentadien}}$$

where $R = H$ or CH_3.

It should be noted that cyclopentane and methylcyclopentane at 600° in the absence of activated carbon did not undergo dehydrogenation, whereas the products of the thermal transformations of cyclohexane and methylcyclohexane at the same temperature contained the corresponding aromatic hydrocarbons in an amount of 6%. Comparison of the results of the thermal transformations of cyclanes with the extent of their conversion in the presence of active birch carbon indicates the high activity of the latter in carrying out the dehydrogenation reaction of five- and six-membered cyclanes.

Experimental Part

Starting hydrocarbons

Cyclopentane, b.p. 49.5°/754 mm, n_D^{20} 1.4070 and d_4^{20} 0.7459, was obtained by hydrogenation of cyclopentene, which in turn was prepared from cyclopentanol by dehydrating it over anhydrous magnesium sulfate at 310°:

$$\text{cyclopentanol} \xrightarrow[(\text{MgSO}_4)]{310^\circ} \text{cyclopentene} \xrightarrow[\text{skeleton Ni–Al}]{170^\circ,\ \text{H}_2} \text{cyclopentane}$$

Methylcyclopentane, b.p. 72°/759 mm, n_D^{20} 1.4100 and d_4^{20} 0.7492, was obtained as a result of the isomerization of cyclohexane (b.p. 80.8°/758 mm, n_D^{20} 1.4262, d_4^{20} 0.7787) under conditions of continuous slow distillation on a column of efficiency 20 theoretical plates over aluminum chloride.

Methylcyclohexane had b.p. 101°/757 mm, n_D^{20} 1.4231 and d_4^{20} 0.7698.

The catalyst used was wood activated carbon from the Perm plant, with a specific surface area of 519 m^2/g and an ash content of 0.48%.

In experiments carried out in the absence of carbon, the glass tube was filled with pieces of crushed quartz. The starting hydrocarbons were fed in portions

Table 1

Dehydrogenation of five- and six-membered cyclanes on activated carbon

Starting cyclane	Pressure, mm Hg	Temp., °C	Feed rate, h^{-1}	Catalyst yield, %	n_D^{20} of catalyzate	Content in catalyzate of dehydrogenation products, %
Catalyst — birch carbon from the Perm plant						
Cyclopentane	10	550	0.1	84.0	1.4140	14
»	10	600	0.1	81.7	1.4180	18
Methylcyclopentane	10	500	0.1	90.2	1.4230	11
»	12	550	0.1	89.4	1.4245	16
»	15	600	0.1	84.1	1.4295	29
Cyclohexane	755	500	0.3	80.4	1.4723	70
»	754	500	0.1	79.9	1.4775	76
»	754	550	0.1	79.0	1.4808	82
»	756	600	0.3	76.1	1.4940	93
»	754	600	0.1	75.3	1.4977	97
Methylcyclohexane	756	500	0.1	81.2	1.4518	44
»	756	550	0.1	74.2	1.4935	95
»	756	600	0.1	74.8	1.4970	100
In the absence of catalyst						
Cyclopentane	15	600	0.1	90.9	1.4070	0
Methylcyclopentane	15	600	0.1	88.1	1.4100	0
Cyclohexane	758	550	0.1	77.9	1.4262	0
»	758	600	0.1	74.3	1.4290	6
Methylcyclohexane	750	500	0.1	81.2	1.4233	0
»	750	550	0.1	71.5	1.4242	2
»	750	600	0.1	70.1	1.4265	6

in 10-ml portions at a rate of 0.3—0.1 h^{-1}. In the dehydrogenation products of the five-membered cyclanes, immediately after the experiments were performed, the content of cyclopentadiene hydrocarbons was determined by a colorimetric method ([9]). The content of aromatic hydrocarbons in the catalyzates of cyclohexane and methylcyclohexane, after distillation over sodium, was determined by a refractometric method ([10]).

The results of experiments on the dehydrogenation of five- and six-membered cyclanes in the presence of birch activated carbon are presented in Table 1.

From the data presented it is evident that cyclopentane and methylcyclopentane are dehydrogenated to the corresponding cyclopentadiene hydrocarbons, the content of which in the catalyzate obtained in the experiment at 600°, with a feed rate of the initial hydrocarbon of 0.1 h^{-1} and with the pressure reduced to 10-15 mm, is 18 and 29%, respectively. The extent of dehydrogenation of cyclohexane and methylcyclohexane to aromatic hydrocarbons at the same temperature, but at ordinary pressure, reaches 97-100%; the yield of catalyzate in this case is 75.3 and 74.8%. Dehydrogenation of cyclohexane at 500° and a space velocity of 0.3 gives a catalyzate containing 70.0% benzene, while at 600° and with the same threefold space velocity the benzene content in the catalyzate reaches 93%. From the experimental results it is also evident that the temperature factor has a considerable effect on the yield of dehydrogenation products. Thus, with an increase in temperature from 500 to 600° the yield of aromatic hydrocarbons in the dehydrogenation reaction of cyclohexane increases by 23-21%, and the degree of dehydrogenation of methylcyclopentane increases more than 2.5-fold. The feed rate of the initial hydrocarbon plays a smaller role in the dehydrogenation reaction of cyclanes: with a threefold decrease in the space velocity of cyclohexane feed—from 0.3 h^{-1} to 0.1 h^{-1}—the benzene content increases only from 93 to 97%.

It should be noted that in the cyclohexane catalyzate (b.p. 78-80° at 759 mm, n_D^{20} 1.4979, d_4^{20} 0.8768), obtained in experiments at 600°, in addition to benzene, only the initial cyclohexane in an amount of about 3% was detected by gas-liquid chromatography. At the same time, in the methylcyclohexane catalyzate (b.p. 90-110° at 752 mm, n_D^{20} 1.4970, d_4^{20} 0.8728), together with toluene, up to 20% benzene was found. This experimental fact indicates that, under the selected conditions, a side reaction of demethylation of toluene to benzene takes place. In subsequent work we shall investigate in greater detail the catalytic action of activated carbon.

Experiments with cyclanes, carried out for comparison in the absence of a catalyst, showed that at 600° cyclopentane and methylcyclopentane do not undergo dehydrogenation to any appreciable extent. Cyclohexane, passed through under thermal conditions at 550°, also left the reaction zone unchanged; however, the cyclohexane condensate collected in the experiment conducted at 600° contained 6% benzene. At the same time, toluene was detected in the methylcyclohexane condensate already in experiments at 550°, although in an insignificant amount —about 2%; in experiments at 600° the toluene content in the condensate was

6%.

Thus, as a result of the investigation it has been established that activated birch charcoal possesses the property of carrying out the dehydrogenation reaction of five- and six-membered cyclanes under elevated-temperature conditions, with high yields of dehydrogenation products. At 600° the degree of conversion of cyclohexane and methylcyclohexane into aromatic hydrocarbons reaches 97 and 100%, respectively; cyclopentane and methylcyclopentane under these conditions are converted into the corresponding cyclopentadiene hydrocarbons with yields of the latter up to 29%.

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