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Investigation of the Mechanism of Dehydrogenation of Cyclohexane over Holmium Oxide Using Radiocarbon C-14

In a previous paper [1], the use of radiocarbon C^{14} was described for studying the role of cyclohexene in the dehydrogenation of cyclohexane over chromia and rhenium catalysts. It was found that over a rhenium-on-carbon catalyst at a temperature of 336°, all the benzene is formed directly from cyclohexane. This result confirmed the earlier conclusion [2] regarding the sextet mechanism of cyclohexane dehydrogenation on this catalyst. At the same time it turned out that over a chromia catalyst, for which a doublet mechanism had previously been proposed [3], at 450° a certain portion of the benzene is formed by a consecutive route; however, direct formation of benzene from cyclohexane was also observed.

The present work is devoted to the study of the mechanism of cyclohexane dehydrogenation using radiocarbon C^{14} over holmium oxide. This catalyst carries out the dehydrogenation of cyclohexane only at temperatures above 500°. Thus it was shown [4] that at 530, 560, and 590°, and at a space velocity of 0.25 h^{-1}, over Ho_2O_3 there is obtained, respectively, 9.4, 22.6, and 43.8% benzene. The activation energy, calculated from the temperature dependence of the logarithm of the degree of conversion, was 39 kcal/mol. In the catalyzates, besides cyclohexane and benzene, cyclohexene and methylcyclopentane were detected in small amounts. Such properties of holmium oxide made it possible to suppose that on this catalyst the dehydrogenation of cyclohexane proceeds by a doublet mechanism, and, consequently, benzene is formed by a consecutive route.

Experimental Part

Cyclohexane and labeled cyclohexene were used in the work. The cyclohexane, thoroughly purified, had the constants: n_D^{20} 1.4265, d_4^{20} 0.7781, b.p. 80.8°. Cyclohexene labeled with radiocarbon C^{14}, obtained from labeled phenol, had a specific radioactivity, determined radiochromatographically (see below), of 217 imp/sec per 1 mg of $BaCO_3$.

The method of preparing the catalyst and the apparatus are described in papers [4,1]. In the present work 6 ml of catalyst (5.0 g) was used; the catalyst grains had a size of 1–2 mm. The surface area of the catalyst, determined chromato-

graphically from the adsorption of nitrogen from a mixture with helium by the method [5], was 46 m^2/g.**

Before each experiment cyclohexane was passed over the catalyst until a constant activity was reached (usually 2–3 hours); to monitor the activity, the refractive index of the catalyzate was measured periodically. After this, the feed of cyclohexane was stopped and pure argon was passed through the tube with the catalyst for 15 min at a rate of 20 ml/min, after which the experiment was carried out. During the experiment, usually 2–3 ml

* O. K. Shchukina took part in the work.
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of the initial hydrocarbon mixture; the first half of the catalyst was discarded, and the second was collected and analyzed. After the experiment the catalyst was regenerated by passing a mixture of air with nitrogen, as described in (4), for 6 h.

The activity of the catalyst treated in this way was readily reproduced. Thus, in three experiments, cyclohexane was passed over the catalyst at 560° with a space velocity of 1.07 h^{-1}. After 2.5 h in the first two experiments and after 2 h in the third experiment, the refractive indices of the catalyst were, respectively, 1.4321, 1.4319, and 1.4321. This refractive index was maintained, to within two units in the last digit, over the subsequent 2–4 h during which the experiments were carried out.

In a special series of experiments it was found that, when a mixture of cyclohexane and cyclohexene containing $\sim 5\%$ of the latter was passed over holmium oxide at 560°, at a space velocity from 0.6 to 2.5 h^{-1}, the catalyzates contained cyclohexene and benzene in amounts sufficient for reliable determination of their concentrations and radioactivities. Therefore, for the study of the dehydrogenation mechanism, cyclohexane with an addition of 4.3 mole % labeled cyclohexene was used.

Table 1

Dehydrogenation of a mixture of cyclohexane and labeled cyclohexene (4.3 mole %) over holmium oxide; amount of catalyst 6 ml; temperature 560°

$1/n_0$	Yield (in mole fractions) —cyclohexadiene	Yield (in mole fractions) —cyclohexane	Yield (in mole fractions) —cyclohexene	Yield (in mole fractions) —benzene	Specific radioactivities (in % of the specific radioactivity of the initial cyclohexene) —cyclohexane	Specific radioactivities (in % of the specific radioactivity of the initial cyclohexene) —cyclohexene	Specific radioactivities (in % of the specific radioactivity of the initial cyclohexene) —benzene
11.1	–	0.804	0.037	0.030	0.0	49.3	41.9
27.4	0.002	0.637	0.027	0.044	0.0	32.9	31.1
31.8	0.004	0.778	0.040	0.059	0.0	27.0	26.5
53.2	0.005	0.694	0.029	0.091	0.0	12.2	19.5
68.1	0.005	0.731	0.035	0.099	0.0	10.5	19.3
94.5	0.008	0.605	0.033	0.118	0.0	7.5	14.4

Note. In view of the low content of methylcyclopentane in the catalyzates, its radioactivity was not calculated.

Analyses of liquid catalyzates were carried out on the radiochromatograph described in (6). Benzene with a specific radioactivity, determined as barium carbonate, of 64 counts/sec per 1 mg of $BaCO_3$ was used as the radioactivity standard. For separation, a copper column 9 m long, with an internal diameter of 2 mm, was used; it was packed with refractory brick (particle size 0.25-0.4 mm), treated with "aqua regia" according to the procedure of (7), onto which ether of triethylene glycol and *n*-butyric acid had been deposited in an amount of 22.4 wt.%. The separation was carried out at a column temperature of 65° and a helium flow rate of 20 ml/min. Figure 1 gives, as an example, a radiochromatogram of a catalyzate obtained in one of the experiments.

Chromatographic analyses of the gases were carried out* in two experiments, at the maximum and minimum feed rates of the mixture. The hydrogen content was, respectively, 86.7 and 79.8%; the principal portion of the by-products consisted of ethane (up to 5%), ethylene (up to 4.9%), and propylene (up to 4%).

The results of experiments with a mixture of cyclohexane and labeled cyclohexene are presented in Table 1.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Processing of the Results and Discussion

In view of the fact that dehydrogenation of the cyclohexane-cyclohexene mixture over holmium oxide is accompanied by substantial coke formation, the scheme given in (1) should be supplemented by the corresponding pro-

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processes proceeding with rates w_4, w_5, and w_6, after which it takes the form:

$$\begin{array}{ccc} \mathrm{C_6H_{12}} & \underset{w_1'}{\overset{w}{\rightleftharpoons}} & \mathrm{C_6H_{10}} \\ \downarrow w_5 & & \downarrow w_6 \\ & \mathrm{C_6H_6} & \\ \searrow w_2 & \downarrow w_4 & \swarrow w_3 \\ & \mathrm{Coke} & \end{array}$$

Calculation of the rates of scheme (1) requires knowledge of the specific radioactivity and the amount of coke formed during the experiment. Accurate determination of these quantities did not appear possible, since the main mass of coke was obtained not during the experiment itself, but while bringing the catalyst to constant activity. Therefore we decided to limit our task to finding the ratio of the rates w_2 and w_3, which determines the pathways of benzene formation under the experimental conditions. For this purpose one may use equation (8):

$$\gamma \approx n_0 \left[x \int_0^{1/n_0} \alpha \, d\left(\frac{1}{n_0}\right) + (1-x) \int_0^{1/n_0} \beta \, d\left(\frac{1}{n_0}\right) \right], \qquad (2)$$

where n_0 is the flow rate (in millimoles per second), $x = w_2/(w_2 + w_3)$, α is the specific radioactivity of cyclohexane, β that of cyclohexene, and γ that of benzene.

Fig. 1. Radiochromatogram of the catalyst obtained in one of the experiments. *A*—concentrations, *B*—radioactivities of the reaction products. The numbers denote: 1—methylcyclopentane, 2—cyclohexane, 3—cyclohexene, 4—benzene.

Fig. 2. Dependence of the specific radioactivity of benzene γ on the flow rate of a mixture of cyclohexane and labeled cyclohexene. *A*—$\mathrm{Ho_2O_3}$ (6 ml), 560°,

content of labeled cyclohexene in the initial mixture 4.3 mol.%: a–experimental data, b–calculated at $x = 0.45$, v–calculated at $x = 0.60$, g–calculated at $x = 0.30$. B–Cr_2O_3 (5 ml), 450°, content of labeled cyclohexene in the initial mixture 7.7 mol.%: a–experimental data, b–calculated at $x = 0.53$, v–calculated at $x = 0.65$, g–calculated at $x = 0.40$. V–Re/C (5 ml), 336°, content of labeled cyclohexene in the initial mixture 9.0 mol.%: a–experimental data, b–calculated at $x = 0.94$, v–calculated at $x = 0.80$.

Using equation (2), one can obtain the values of γ for different x and $\frac{1}{n_0}$ (the numerical values of the integrals can be found approximately from plots of the dependence of α and β on $\frac{1}{n_0}$).

In Fig. 2A the values obtained in the experiments and calculated from equation (2) are shown. As can be seen from the figure, at $x = 0.45$ the calculated and experimental values fall well on a single curve. Thus, on holmium oxide at 560° the fraction of benzene formed by the consecutive route is somewhat greater than on chromium oxide at 450° in work ([1]).

For a more visual comparison it seemed of interest to process, by equation (2), the data from work ([1]), obtained for the chromia and rhenium catalysts*. In doing so it must be taken into account that the values of x obtained from equation (2) are averaged over the entire interval of space velocities used and, consequently, they should not coincide with the ratios of rates found in work ([1]).

In Figs. 2B and 2C the calculated values of γ are compared with the experimental values taken from work ([1]). For the chromia catalyst, on which the ratio of the rates w_2 and w_3 changes little when the space velocity is varied, the points calculated at $x = 0.53$ fall well on the experimental curve. For the rhenium catalyst, values of γ close to the experimental ones are obtained at $x = 0.94$, which agrees with the conclusions of work ([1]). The poorer agreement between the calculated values of γ and those found experimentally in this case is apparently due to the fact that, on the rhenium catalyst, the ratio of the rates w_2 and w_3 depends strongly on the space velocity (see Table 4 of work ([1])).

As already indicated, the consecutive route of benzene formation from cyclohexane must occur under a doublet mechanism; therefore, the experimental confirmation that benzene on holmium oxide and on chromium oxide is formed to a certain extent through cyclohexene indicates that, on these catalysts, the dehydrogenation of cyclohexane can proceed, at least in part, by a doublet mechanism.

As for the "direct" formation of benzene from cyclohexane on the same catalysts, which we observed in the present work and in work ([1]), its explanation may involve a sextet mechanism, analogous to that used in explaining the properties of vanadium oxide ([9]) and chromia ([10]) catalysts, or the assumption that, in this case, dehydrogenation of cyclohexane proceeds with intermediate formation of cyclohexene and, possibly, cyclohexadiene, but without their desorption into the

gas phase. Owing to the rapid course of the intermediate stages under such a mechanism, the reaction taking place on an active center consisting, for example, of two catalyst atoms may have the external features of a sextet mechanism.

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* We take this opportunity to note that in work ([1]) the chromia and rhenium catalysts were used in amounts of 5 ml each.

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