G. V. ISAGULYANTS, E. N. KOMAROVA, Academician A. A. BALANDIN

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Abstract

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G. V. ISAGULYANTS, E. N. KOMAROVA, Academician A. A. BALANDIN

ON THE MECHANISM OF DEHYDROGENATION OF SIX-MEMBERED CYCLANES.

DEHYDROGENATION OF METHYLCYCLOHEXANE

ON AN ALUMINA-CHROMIA CATALYST

It was shown earlier, by the use of the tracer-atom method, that in the dehydrogenation of cyclohexane on chromium oxide ([1]) and on holmium oxide ([2]), cyclohexene is the immediate precursor of benzene. These data are of definite significance for ideas concerning the mechanism of hydro-dehydrogenation. It is no accident that a number of authors ([3,4]) have recently been employing new methods to elucidate the role of cycloolefins, in particular in the hydrogenation reaction of aromatic hydrocarbons. It is therefore of interest to extend the data obtained by us to a broader range of objects. In the present work we studied the pathways of formation of aromatic hydrocarbons from cyclanes on an oxidic alumina-chromia catalyst, using methylcyclohexane as an example.

Using additions of labeled methylcyclohexene, we investigated the ratios of the rates in Scheme 1, as was done in the cited work ([1]).

$$\begin{tikzcd}
C_7H_{14} \arrow[rr, shift left, "W_1"] \arrow[dr, "W_3"'] & & C_7H_{12} \arrow[ll, shift left, "W_1'"] \arrow[dl, "W_2"] \\
& C_7H_8 &
\end{tikzcd}$$

Scheme 1

Starting materials. Methylcyclohexane (commercial), after distillation, had a boiling point of 100.1° (742 mm); d_4^{20} 0.770; n_D^{20} 1.4235. Methylcyclohexene, synthesized by the method of ([5]), had a boiling point of 109° (745 mm); n_D^{20} 1.4506. Radioactive methylcyclohexene (commercial), after dilution with synthesized nonradioactive material, had a specific radioactivity of 53 impulses/sec · mg $BaCO_3$.

Fig. 1. Dependence of the degree of conversion of cyclohexane to benzene on temperature for samples with grain sizes of 3 and 1 mm

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Experimental procedure. The experiments were carried out in a flow apparatus with a small-volume vertical reactor; the vapors of the starting material were fed from below by means of an automatic burette and heated to the reaction temperature while passing through a long coil. The temperature in the catalyst bed was measured with a thermocouple, and its fluctuations did not exceed $\pm 2^{\circ}$. The liquid catalyzate was collected in a receiver with a reflux condenser cooled by running water. The gas was collected in a calibrated gasometer over a sodium chloride solution. For analysis, catalyzates were collected 30 min after the start of the experiment, when a steady state had been established.

Analysis. Analysis of the liquid products was carried out on the SKB chromatograph of our institute. A copper spiral column 4 m long with an internal diameter of 6 mm was used, packed with diatomaceous brick containing 5% (by weight of the brick) β, β'-dioxidipropionitrile as the liquid phase.

After passing through the column, the fractions entered a tube with copper oxide, heated to 750–800°, where they were burned to CO_2. The carbon dioxide formed was fed to the chromatograph detector (catharometer) and then into bubblers with baryta water. The carbonate precipitates obtained for radiometric analysis were treated and deposited on targets as in work ([1]). Special attention was paid to the identity of the conditions under which the targets were prepared. To determine the radioactivity, an end-window counter and a PS-5M apparatus were used. The corresponding correction for self-absorption was made. From each precipitate no fewer than 4 targets were made, and the mean value was used in the calculations.

Gas analysis was carried out on an improved Orsa apparatus; usually the gas consisted of not less than 98% hydrogen. All starting substances were also subjected to chromatographic analysis. Methylcyclohexane had a high degree of purity; methylcyclohexene-1 contained about 1% of a more volatile product (see Fig. 2), which we took to be an isomer with a different position of the double bond.

Fig. 1. Dependence of the degree of conversion of cyclohexane to benzene on temperature for samples with grain sizes of 3 and 1 mm.

Catalyst—chromium oxide (15%) on aluminum oxide (82%) with an addition of potassium oxide (3%). Catalysts of this type are usually used in dehydrogenation and aromatization reactions of alkanes and have been studied in detail in a number of works ([7,8]). It is known that initially they do not possess stable activity and are usually "developed" under reaction conditions. For our catalyst samples we achieved standard activity by passing *n*-heptane at a space velocity of 0.3 h^{-1} for 6 hours at 500° (with subsequent blowing with air for 3 hours).

After such treatment the catalyst has well reproducible activity (between experiments hydrogen was passed over the catalyst). This was established in a series of experiments on the dehydrogenation of cyclohexane, some of which were also set up in order to determine the influence of diffusion retardation on the dehydrogenation of cyclanes.

Preliminary experiments with cyclohexane were carried out in the temperature range 490—520° at a space velocity of 1 h^{-1} on two catalyst samples with sizes of 1 and 3 mm (the degree of conversion of cyclohexane to benzene was monitored by the refractive index).

The results are given in Fig. 1. For both samples the points lie on one straight line, which may serve as an indication that, under the conditions considered, dehydrogenation proceeds in the kinetic region. The "apparent activation energy" calculated from the temperature dependence of the degree of conversion proved to be 17.3 kcal/mol.

Table 1

Dehydrogenation of methylcyclohexane on the catalyst Cr_2O_3/Al_2O_3

Contact time	Temp. of experiments, °C	methylcyclohexane	methylcyclohexene	toluene	Apparent activation energy, kcal/mol
19.3	470	75.4	2.6	21.3	21 520
19.3	490	69.8	2.6	27.7	21 520
19.3	500	60.1	3.6	35.8	21 520
19.3	510	52.4	2.8	43.9	21 520
19.3	520	46.2	2.4	50.7	21 520
46.3	470	70.9	4.1	24.1	21 520
46.3	490	58.8	5.4	35.1	21 520
46.3	500	51.4	4.7	41.9	21 520
46.3	520	30.5	4.3	65	21 520

Dehydrogenation of methylcyclohexane was carried out on a catalyst with a grain size of 1 mm and at two space velocities, 1.0 and 0.43 hr^{-1} (catalyst volume 3 ml). The catalyzates consisted of methylcyclohexane, isomeric methylcyclohexenes, and toluene.

The experimental results are given in Table 1. As was observed earlier, the concentration of the cycloolefin has a maximum at a degree of conversion of the cyclane

[Figure 2 and Figure 3]

Fig. 2. Change in concentrations as a function of contact time (τ):
1—C_1 –methylcyclohexane,
2—C_2 –methylcyclohexene,
3—C_3 –toluene

Fig. 3. Change in specific radioactivities, in percent of the initial value, as a function of τ:
1 –α-methylcyclohexane,
2 –β-methylcyclohexene,
3 –γ-toluene

of about 40%, which corresponds to a temperature of 500° at the higher space velocity and 490° at the lower one (methylcyclohexadiene could not be detected in the catalyzates). The value of the apparent activation energy proved to be 21.5 kcal/mol.

Dehydrogenation of methylcyclohexane with additions of labeled methylcyclohexene. To determine the genetic relationships between methylcyclohexane, methylcyclohexene, and toluene, a series of experiments was carried out on the dehydrogenation of methylcyclohexane with additions of 3% labeled methylcyclohexene.

The radioactivity of the labeled methylcyclohexene isolated from the initial mixture by the method we used coincided with the specific radioactivity of the initial methylcyclohexene; a small activity entered the methylcyclohexane. Below we give the specific radioactivity of the components of the initial mixture after separation on the chromatograph: methylcyclohexane –26.6 imp per 100 sec per 1 ml $BaCO_3$; methylcyclohexene –5210 imp per 100 sec per 1 ml $BaCO_3$. The experiments were carried out at 500° and at various space velocities. The results of the experiments are shown in Figs. 2 and 3. The contact time was determined by the formula

$$\tau = t \cdot b/v,$$

where t is the duration of the experiment in seconds, b is the volume of catalyst, and v is the volume of the initial mixture in milliliters of vapor (N.T.P.).

[Figure 4]

Fig. 4. Dependence of the reaction rates according to scheme 1 on contact time (τ):
1 –sum of the rates of toluene formation,
2 –rate of toluene formation through methylcyclohexene (w_2)

As can be seen from Fig. 4, the specific radioactivity of methylcyclohexane is very low and did not differ from the radioactivity obtained upon separation of the initial mixture. This indicates the absence of a hydrogenation reaction—

of methylcyclohexene or toluene, and also to the absence of the reaction of irreversible catalysis of methylcyclohexene. Using equations obtained on the basis of the kinetic method of labeled-atom application, the rates of formation of the individual products according to Scheme 1 were calculated. The rate of dehydrogenation of methylcyclohexane to methylcyclohexene (w_1) and the rate of dehydrogenation of the latter to toluene over the entire interval τ proved to be close, which is in agreement with the more or less constant concentration of methylcyclohexene in the catalyzates.

Of considerable interest is a comparison of the rate of dehydrogenation of methylcyclohexane (w_2) and of the formation of toluene ($w_2 + w_3$). Both quantities are given graphically in Fig. 4. The total curve for toluene formation is only slightly shifted upward relative to the curve for dehydrogenation of methylcyclohexane; moreover, the fraction of toluene formed via methylcyclohexene amounts to about 70%.

The dehydrogenation of methylcyclohexane in a flow system on an alumina-chromia catalyst was investigated using a chromatographic method for analyzing the reaction products. Radiocarbon-labeled methylcyclohexene was used to determine the genetic relationships among methylcyclohexane, methylcyclohexene, and toluene.

It is shown that up to 70% of the toluene is formed by a route in which methylcyclohexene is its immediate precursor.

Irreversible catalysis of methylcyclohexene was not observed under the experimental conditions.

Institute of Organic Chemistry
named after N. D. Zelinskii
Academy of Sciences of the USSR

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