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I. V. KALECHITS, V. G. LIPOVICH, and V. V. VYKHOVANETS

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Abstract

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I. V. KALECHITS, V. G. LIPOVICH, and V. V. VYKHOVANETS

STUDY OF THE MECHANISM OF DESTRUCTIVE HYDROGENATION OF BENZENE USING LABELED ATOMS

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In the hydrogenation of aromatic hydrocarbons in the presence of industrial sulfide catalysts under conditions of high pressures and temperatures, as is known, not only hydrogenation reactions proper take place, but also reactions of isomerization and cleavage ([1,2]). With increasing contact time, the concentrations of the reaction products change in such a way that, as a first approximation, the process may be represented by a scheme of consecutive reactions ([3]):

$$\text{benzene} \longrightarrow \text{cyclohexane} \longrightarrow \text{methylcyclopentane} \longrightarrow \text{cleavage products} \quad (1)$$

However, this scheme does not reflect the established views on isomerization as a dehydrohydrogenation reaction ([3]), according to which it is not cyclohexane but cyclohexene that should undergo isomerization. Since the latter can be formed in the stepwise hydrogenation of benzene by the doublet mechanism ([5]), a scheme of transformations was proposed ([6])

$$\left.\begin{array}{ll}\text{benzene} \rightleftarrows \text{cyclohexadiene} \rightleftarrows \text{cyclohexene} \rightleftarrows \text{cyclohexane} & (a)\\ \text{cyclohexene} \rightleftarrows \text{methylcyclopentene} \longrightarrow \text{cleavage products} & (b)\end{array}\right\} \quad (2)$$

which, in addition to hydrogenation (a) and isomerization (b), assumes the possibility of the direct formation of methylcyclopentane from benzene (a hydroisomerization reaction, path b).

To test this assumption, experiments were carried out on the hydrogenation of mixtures of benzene and cyclohexane (1 : 1), in which one of the components was labeled with the radioactive isotope C^{14}. Hydrogenation was conducted in a two-liter autoclave in the presence of an industrial WS_2 catalyst at 420±2°C and an initial pressure of 140 atm. To prevent the process from being complicated by various secondary reactions, the autoclave was heated to 420°, after which it was rapidly cooled in a bath with running water. In experiment 11, for comparison, the working temperature was maintained for 3 hours. To confirm the formation of cyclohexene as an intermediate product, in two experiments (19 and 22), when the working temperature was reached, a small amount of labeled cyclohexene was added to the mixture by means of a special device. The individual composition of the hydrogenates was established by chromatographic separation and rectification on a column with an efficiency of 60 theoretical plates (Table 1).

In experiments with labeled benzene, especially at short duration, the specific radioactivity of methylcyclopentane was considerably higher than that of cyclohexane (experiments 15 and 23), whereas in experiments with labeled cyclohexane—

Table 1

Material balances and radioactivity balances of destructive hydrogenation experiments

<table>
<tr><th>Experiment No.</th><th>Indicators</th><th>Introduced: benzene</th><th>Introduced: cyclohexane</th><th>Introduced: methylcyclopentane</th><th>Withdrawn: benzene</th><th>Withdrawn: cyclohexane</th><th>Withdrawn: methylcyclopentane</th><th>Withdrawn: [[unclear: structural formula]]</th><th>Hexanes + pentanes</th><th>Gas + losses</th></tr>
<tr><td>11*</td><td>Material balance, g</td><td>85.6</td><td>77.9</td><td>–</td><td>3.3</td><td>50.7</td><td>–</td><td>69.0</td><td>25.2</td><td>15.3</td></tr>
<tr><td>11*</td><td>Specific radioactivity, % of initial</td><td>100</td><td>–</td><td>–</td><td>98$±2|43±~~2~~|—|50±4|66±4|—||11∗ |Distributionoftotalactivity,±3|19±1|—|65±1|85±1|—||15|Distributiono ∗|Distributionoftotalactivity,±2|9±1|—|49±2|62±2|—||23|Distributiono</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

Experiment No.	Indicators	Introduced: benzene	Introduced: cyclohexane	Introduced: methylcyclopentane	Withdrawn: benzene	Withdrawn: cyclohexane	Withdrawn: methylcyclopentane	Withdrawn: [[unclear: structural formula]]	Hexanes + pentanes	Gas + losses
24	Distribution of total activity, % of initial	–	100	–	0	90.7	–	5.5	0.7	3.1

* Duration of experiment: 3 hours.
** Experiment without catalyst.

lower (experiments 17 and 24). This proves that a significant part of the methylcyclopentane is formed directly from benzene, without desorption from the catalyst surface. At a long contact time (experiment 11), the specific activities come closer together, but nevertheless more activity passes into methylcyclopentane than into cyclohexane. The data of Table 1 also make it possible to explain the apparent consecutiveness of the process (3): at a short contact time, when the concentrations of benzene and cyclohexane are close, most of the benzene is converted into cyclohexane (i.e., path a of scheme (2) predominates), since the latter contains most of the activity of the converted benzene; at the same time, the hydroisomerization reaction proceeds (path b). At a long contact time, as benzene is consumed, its conversion into methylcyclopentane begins to predominate and, in addition, the latter begins to be formed in ever larger amounts from cyclohexane (path c), owing to which the specific activities are equalized.

The data of the material balance and radioactivity balance make it possible to estimate approximately the ratio between the intensities of the named transformations at the moment when the concentrations of benzene and cyclohexane are close to one another.

Denoting the fractions of moles reacting along the possible pathways,

[scheme showing benzene → cyclohexane (x), benzene → methylcyclopentane (y), cyclohexane → methylcyclopentane (z), and methylcyclopentane → cleavage products (u)]

through x, y, z, u, one may assume: $x + y$ is the amount of benzene converted, $x - z$ is the amount of newly formed cyclohexane, $y + z - u$ is the amount of methylcyclopentane formed, x/y is the ratio of the fractions of radioactivity of cyclohexane and methylcyclopentane in experiments with labeled benzene, and z is the fraction of activity transferred to methylcyclopentane and cleavage products in experiments with labeled cyclohexane (Table 2). The data of Table 2 reveal satisfactory qualitative agreement of the results and confirm the process scheme set out above: hydrogenation proceeds fastest of all (path a), followed by hydroisomerization (path b), and isomerization (path c) is somewhat slower. Under the given conditions, cleavage proceeds most slowly.

Table 2

Intensities of individual reactions (g/mol)

Reaction	Experiments with labeled benzene	Experiments with labeled benzene	Experiments with labeled cyclohexane	Experiments with labeled cyclohexane
	15	23	17	24
Hydrogenation of benzene to cyclohexane (x)	0.239	0.218	0.454	0.270
Hydroisomerization of benzene to methylcyclopentane (y)	0.149	0.176	0.134	0.134
Isomerization of cyclohexane (z)	0.106	0.047	0.082	0.067
Cleavage of methylcyclopentane (u)	0.015	0.028	0.028	0.011

Experiments with the addition of labeled cyclohexane support the view of it as an intermediate product. Owing to the high reactivity of cyclohexene, almost 3/4 of which undergoes hydrogenation even in the absence of a catalyst (experiment 22), it should be assumed that in experiment 23 only a very small part of it was converted by the catalytic route; nevertheless, 10.7% of the introduced activity passed into methylcyclopentane. Two further regularities should also be noted: the specific activities of the liquid cleavage products are always higher than those of methylcyclopentane, which indicates an isotope effect, and the changes in the specific activities of methylcyclopentane and of the cleavage products are correlated, whereas there is no relation between the specific activities of cyclohexane and the cleavage products. This supports the view that direct cleavage of cyclohexane without its intermediate isomerization to methylcyclopentane is improbable, as was suggested earlier[7] on the basis of data on the composition of hydrogenation products of individual hydrocarbons.

Eastern Siberian Branch
of the Academy of Sciences of the USSR

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