

MECHANISM FOR THE AROMATIZATION OF N-HEXANE
ON AN ALUMINA-CHROMIUM-IRON CATALYSTG. V. Isagulyants, M. I. Rozengart,
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UDC 541.124:542.97:547.216

The aromatization of paraffins on alumina-chromium-potassium and other oxide catalysts proceeds through the consecutive dehydrogenation of the aliphatic molecule with thermal cyclization at the triene stage [1, 2]. This scheme for the formation of aromatic hydrocarbons does not involve the catalytic cyclization of the paraffin or olefin to yield cyclohexane. Experimental attempts to demonstrate the possibility of such a cyclization on oxide catalysts have not been successful [3]. The formation of cyclopentane hydrocarbons from paraffins, which is a common reaction of metallic catalysts, is only rarely seen on oxide catalysts [4]. An unusual result was obtained in a study of the aromatization of n-hexane on an alumina-chromium-iron catalyst not containing alkali [5]: in addition to hexenes, small amounts of cyclohexane and methylcyclopentane were found in the catalysates, while hexadienes were not seen. On this basis, Krzywicki et al. [5] concluded that the aromatization proceeds exclusively through the formation of a cyclohexane directly from the paraffin or olefin.

EXPERIMENTAL

We used a microcatalytic pulse system [1]. The catalysate was analyzed on a chromatography column packed with 8% triethylene glycol dibutyrate (TEGDB) on Celite 545. The catalyst was prepared as described by Krzywicki et al. [5]. A fraction with 0.25-0.5 mm particle size was taken for the experiments. Weighed catalyst batches from 2 to 200 mg were used. The contact time was considered proportional to the catalyst weight. The experimental temperature was 530°C and the helium gas carrier flow rate was 60 ml/min.

RESULTS AND DISCUSSION

As might have been expected, dehydrogenation products of the starting hydrocarbon are invariably in the catalysates obtained in the aromatization of hexane, 1-hexene, and 1,5-hexadiene. Thus, hexenes are always found in the catalysates of hexane (and even up to 0.2% hexadienes)*, while hexadienes are found in the 1-hexene catalysates and hexatriene is found in the 1,5-hexadiene catalysates, though in extremely small amounts. In addition, hydrogenation products were inevitably found in the catalysates of the unsaturated hydrocarbons for all contact times studied, apparently by means of hydrogen liberated in the aromatization. Thus, 1-hexenes contain up to 5.5% hexane and isohexanes, while 1,5-hexadiene catalysates contain up to 11.8% olefins.

Figure 1 shows that for short contact times, the amount of hexenes in the n-hexane catalysates significantly exceeds the amount of benzene. With an increase in contact time, the curve for the hexene content passes through a maximum and the curve for benzene content is sigmoidal. The same characteristics of a consecutive reaction are also observed in the aromatization of 1-hexene (Fig. 2). It was impossible to study the dependence of the triene content on the contact time in 1,5-hexadiene catalysates in light of the low triene concentration. Since the sequence of the conversions of hexadiene to hexatriene and then to benzene on oxide catalysts has been studied satisfactorily [2], we may reliably assume that hexatriene is also an intermediate in the aromatization in this case as well.

Thus, the behavior demonstrated by the increase in the content of hexenes in n-hexane catalysates and of hexadienes in the hexene catalysates clearly indicates the sequence of conversions: hexane \longrightarrow hexenes \longrightarrow hexadienes \longrightarrow benzene, in accord with the known mechanism [1, 2]. The increase in the benzene content in the catalysates in going from hexene to hexene and hexadiene (for example, from 6.8% to 40.5% and 62.6%) also indicates a mechanism involving the consecutive dehydrogenation of the aliphatic molecule.

The hexene and hexadiene catalysates also contain some quantities of isoolefins and isodienes (for example, up to 1.2 and 3%, respectively, in hexene catalysates) which are nevertheless higher than under the same conditions on an alumina-chromium-potassium catalyst [6]. The hexane catalysates do not contain cyclic products other than benzene. However,

*Krzywicki et al. [5] may have been unable to detect hexadienes in the catalysates since they carried out the experiments in a flow system with significantly longer contact times than in our work.

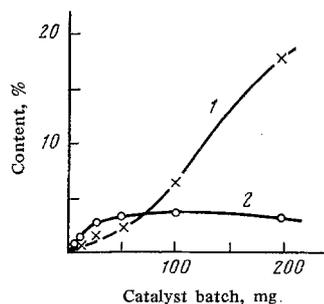


Fig. 1

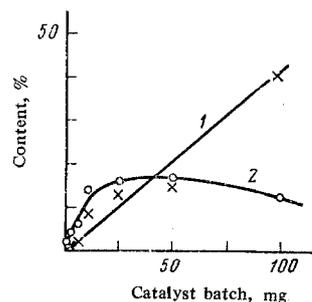


Fig. 2

Fig. 1. Change in the content of hexenes (2) and benzene (1) in catalysates obtained in the aromatization of *n*-hexane on alumina-chromium-iron catalyst with variation in the contact time at 530°C.

Fig. 2. Change in the content of hexadienes (2) and benzene (1) in catalysates obtained in the aromatization of 1-hexene on an alumina-chromium-iron catalyst with variation of contact time at 530°C.

TABLE 1. Benzene Content in the Catalysates of Aromatization of Various C_6 -Hydrocarbons on an Alumina-Chromium-Iron Catalyst in a Pulse Mode (60 ml/min helium flow rate, 100 mg catalyst batch, 530°C)

Starting hydrocarbon	Benzene content, %	Starting hydrocarbon	Benzene content, %
Hexane	6,8	Cyclohexane	33,3
1-Hexene	40,5	Methylcyclopentane	3,0
1,5-Hexadiene	62,5	2-Methylcyclopentene	8,8

the chromatograms of the hexene and hexadiene catalysates show peaks of up to 0.5% corresponding to the retention time for cyclohexane. In addition, up to 0.9% 1-methylcyclopentene and traces of methylcyclopentadienes were found in these catalysates.

In principle, cyclohexane and methylcyclopentane,* similar to hexenes, may be intermediates in the aromatization of hexane if we assume that the conversion of hexane into benzene occurs through C_6 - and C_5 -dehydrocyclization, respectively.† In this case, the small amount or absence of these hydrocarbons in the catalysates may be the result of the higher rate of their conversion into aromatic hydrocarbons than their formation from the paraffin. Then, we should expect that the yield of benzene from cyclohexane or methylcyclopentane under the same conditions will be significantly higher than from hexene.

This hypothesis was checked by a comparison of the reactivities of hydrocarbons which are possible intermediates in the aromatization of *n*-hexane (Table 1). The rate of formation of benzene from cyclohexane is significantly lower than from 1-hexene. Furthermore, hexenes are always present in the catalysates while there is no cyclohexane. Thus, if cyclohexane indeed were formed from hexane, it would be detected in the catalysates. This finding clearly shows that the contribution of cyclohexane as a possible intermediate in the aromatization of hexane is at best a fraction of a percent. This is even more true for the participation of methylcyclopentane since even less benzene is formed from it than from hexane, as seen in Table 1.

CONCLUSIONS

1. The formation of an aromatic hydrocarbon from a paraffin on an alumina-chromium-iron catalyst not containing alkali proceeds through the sequential dehydrogenation of the aliphatic molecule, i.e., through a mechanism which is well known for oxide aromatization catalysts.

2. The contribution of aromatization pathways through the formation of cyclic products in the first reaction steps is either very small or absent completely.

*It is very difficult to detect small amounts of methylcyclopentane on TEGDB. However, the methylcyclopentene peak in the chromatograms also indicates the presence of methylcyclopentane in the catalysate.

†The presence of cyclohexane in the catalysates may be a consequence of the hydrogenation of benzene by hydrogen liberated in the aromatization process.

LITERATURE CITED

1. M. I. Rozengart, G. V. Isagulyants, Yu. G. Dubinskii, L. I. Kovalenko, E. M. Gutkina, and B. A. Kazanskii, *Neftekhimiya*, **14**, 36 (1974).
2. G. V. Isagulyants, M. I. Rozengart, Yu. G. Dubinskii, L. I. Kovalenko, E. M. Gutkina, and B. A. Kazanskii, *Neftekhimiya*, **15**, 505 (1975).
3. V. J. Komarevsky and W. S. Shand, *J. Am. Chem. Soc.*, **66**, 1118 (1944).
4. N. I. Shuikin, E. A. Timofeeva, and T. P. Dobrynina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **572**, 863 (1961).
5. A. Krzywicki, S. Malinowski, and M. Marczewski, *Chem. Stosow.*, **19**, 495 (1975).
6. M. I. Rozengart, G. V. Isagulyants, Yu. G. Dubinskii, L. I. Kovalenko, and V. G. Bryukhanov, *Neftekhimiya*, **16**, 201 (1976).

CARBONYLATION OF BRANCHED OLEFINS IN THE PRESENCE OF $\text{BF}_3 \cdot \text{H}_2\text{O}$ AND ETHYL FORMATE AT ATMOSPHERIC PRESSURE

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UDC 542.97:547.313

Esters of α , α -branched carboxylic acids may be obtained by the carbonylation of olefins with CO in the presence of acidic catalysts at 100-200 atm [1, 2]. This process may also be carried out at atmospheric pressure, using formic acid and sulfuric acid as the source of CO [3] with subsequent treatment of the reaction mixture with water or alcohol in order to decompose the acyl complex $\text{RCO} \cdot \text{H}_2\text{SO}_4$ and the separation of the forming α , α -branched carboxylic acids or their esters. Great interest lies in the one-step preparation of the esters of branched carboxylic acids by the carbonylation of olefins using ethyl formate (EF) as the source of CO and esterification agent in the presence of H_2SO_4 or H_3PO_4 [4, 5].

In the present communication, the results are given for a study of this reaction using the complex of BF_3 with water as the catalyst.

The major products of the carbonylation of 2-methyl-2-butene with EF in the presence of $\text{BF}_3 \cdot \text{H}_2\text{O}$ as the catalyst at atmospheric pressure were the ethyl esters (EE) of α , α -dimethylbutyric (α , α -DMB), α -ethylbutyric (α -EB), and of C_7 , C_8 , and C_9 acids (Table 1). Ethyl trimethylacetate (TMA) was also formed.

Change in the olefin (O1):catalyst (Ct):EF molar ratio affects the yields and composition of the ester products. The greatest ester yield was obtained (49.4%) for O1:Ct:EF = 1:4:8 (see Table 1, experiment 9). Doubling the catalyst concentration (runs 1 and 4) does not lead to a change in the total yield of esters (39%), though it has a significant effect on the product composition. An increase in the EF:Ct molar ratio by a factor of 2-3 (runs 1-3) with O1:Ct = 1:1 leads to an increase in the amount of C_6 acid ethyl esters and equivalent decrease in the ethyl esters of the disproportionation acids (TMA and C_7 - C_9 acids). Similar behavior was found upon increasing the EF:Ct molar ratio by a factor of 2-3 for O1:Ct molar ratio = 1:2 (runs 4-6) and 1:4 (7-9).

Upon increasing the temperature from 20 to 75°C (Table 2), the total ester yield passes through a maximum at 60°C. The content of EE α , α -DMB decreases by more than a factor of 2. The content of EE α -EB drops from 37.0 to 26.5% upon increasing the temperature from 20 to 60°C and then increases to 33.7% at 70°C. The total content of the ethyl esters of the C_6 , C_7 , C_8 , and C_9 disproportionation acids increases from 16% at 20°C to 45% at 70°C. In the case of the carbethoxylation of 2-methyl-2-pentene (Table 3) using EF in the presence of $\text{BF}_3 \cdot \text{H}_2\text{O}$, the yield of ethyl esters increases from 36 to 56% in going from 20 to 80°C and the content of the ethyl esters of the monomeric acids, α , α -dimethylvaleric (α , α -DMV) and α -methyl- α -ethylbutyric (α -M- α -EB) acids passes through a maximum 27.4% at 70°C and 62% at 30°C, respectively. The maximum total yield of the ethyl esters of α , α -DMV and α -M- α -EB is 73% at 30°C.

Examination of the ratio of the yields of the ethyl esters of α , α -DMV and α -M- α -EB with increasing temperature indicates that the ester α , α -DMV is a product of the isomerization of carbocation C which forms from carbocation B or of

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