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Abstract

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ON THE MECHANISM OF THE INTERACTION OF CYCLOHEXANE WITH THE SURFACE OF A METALLIC CATALYST

From the standpoint of the theory of catalyst selection, the question of the mechanism of the interaction of cyclohexane and benzene with the catalyst surface is of considerable interest. Investigations in this direction were begun in studies using the method of deuteroexchange on metals ($^{1-3}$) and on chromium oxide (^{3}). One of the detailed investigations of this question belongs to Anderson and Kemball (^{4}), who studied the exchange reaction of the hydrogen atoms of cyclohexane and cyclopentane for deuterium on evaporated metallic catalysts. On the basis of determining the relative rate of exchange of hydrogen atoms, the authors proposed a mechanism for this reaction. In their opinion, cyclohexane (or cyclopentane) is adsorbed on the surface by two neighboring carbon atoms; then one of the carbon—catalyst bonds is broken and a new bond is formed with the next carbon atom, while the broken bond is saturated by a deuterium atom located on the catalyst surface. This process is then repeated, and a kind of "rolling" of the cyclohexane molecule over the surface takes place. During exchange the first six hydrogen atoms exchange more rapidly than the next six (on the deuterium distribution curve there is a clearly expressed maximum at the sixth atom). The authors believe that exchange occurs first along one side of the ring and then along the other. The transition from one side to the other is hindered, since the cyclohexane molecule must turn over on the catalyst surface, which requires additional energy. An increase in temperature should, in the opinion of Anderson and Kemball, facilitate the turning over of the molecule. Therefore, as the temperature increases, the maximum corresponding to hexadeuterated cyclohexane, $C_6H_6D_6$, should disappear, while the amount of deuterated cyclohexanes with 7–12 deuterium atoms should increase. In the work cited, the reaction was studied only at low temperatures; on platinum, for example, at a temperature not higher than 0°. The dependence of the shape of the distribution curve on temperature was not studied in sufficient detail, and therefore the disappearance of the maximum—at any rate a sufficiently distinct one—was not observed. In subsequent works Kemball and co-workers (^{5}) proposed another explanation for the difficulty of exchange of the second half of the hydrogen atoms, based on the formation of intermediate organometallic compounds with π-bonds of the allylic type.

R. Barel and co-workers (^{6}), who studied the exchange of hydrocarbons with deuterium on palladium catalysts supported on Al_2O_3, observed the disappearance of the maximum at $C_6H_6D_6$ for cyclohexane in the range from 50 to 170°. For cyclopentane, disappearance was likewise observed of the maximum corresponding in this case to pentadeuterated cyclopentane, $C_5H_5D_5$.

In the present work, the effect of temperature on the distribution of deuteroproducts on metallic platinum films was studied specifically. The method of preparing the catalysts and the apparatus scheme were analogous to those described by Ch. Kemball ([7]). The experiments were carried out at a pressure of about 40 mm Hg, with a molar ratio $D_2 : C_6H_{12} \approx 60 : 1$. Analysis of the products was performed on an MI-1305 mass spectrometer, at an ionizing voltage

40 V. In the mass spectrum of the cyclohexane used, no impurities were detected, at least in the mass range 84-96. The deuterium was taken directly from the cylinder and passed only through a trap cooled with liquid nitrogen, since special experiments showed that the results obtained with such deuterium and with deuterium previously passed through a diffusion nickel lamp coincide.

The reaction was studied in the temperature range from 0 to 185°. Typical curves in this range on Pt are shown in Fig. 1. Let us note that the activity of the films, and consequently also the depth of exchange with time, was not constant in all experiments. This, however, in no way affects our conclusions, because in the present case only the character of the distribution is significant, i.e., the relative, and not the absolute, content of one or another deuterated cyclohexane. As can be seen from Fig. 1, a change in temperature does not noticeably affect the form of the distribution curve, and the peak at the sixth atom does not disappear.

It is interesting to note that at a temperature of 100–110° the course of exchange changes. In this narrow temperature interval the amount of highly deuterated products increases appreciably, while products with a low deuterium content decrease relatively, although at a higher temperature the form of the curve again becomes approximately the same as before 100°.

The curves shown in Fig. 1 correspond to the distribution observed 180 minutes after the beginning of exchange. However, as can be seen from Fig. 2, the form of these curves does not undergo any change with time up to a fairly deep conversion, and the peak at the sixth atom is preserved in all cases.

In the present work it was found that on tungsten and iron a different distribution of deuteration products is obtained, without the characteristic peak at the sixth atom (Fig. 3), which should be observed in exchange proceeding according to the Anderson and Kemball scheme. The study of exchange on these metals over a broad temperature range will be the subject of further investigation.

To explain the difference in the character of the product distribution on platinum, on the one hand, and on iron and tungsten, on the other, it may be supposed that the reaction mechanisms on these metals differ from one another.

Fig. 1

Figure 1: Fig. 1

Fig. 2. Dependence of the distribution of deuterocyclohexanes on time on Pt at 63°C; 1 –30 min after the start of exchange, 2 –after 60 min, 3 –after 180 min.

Figure 2: Fig. 2. Dependence of the distribution of deuterocyclohexanes on time on Pt at 63°C; 1 –30 min after the start of exchange, 2 –after 60 min, 3 –after 180 min.

This supposition contradicts the ideas of Anderson and Kemball, who do not take into account the type of crystal lattice and interatomic distances.

Fig. 1. Distribution curves of the products of deuterium exchange of cyclohexane at different temperatures on Pt (ordinate axis—the relative value of the content of deutero-cyclohexanes; the amount of cyclohexane $C_6H_{11}D$ is taken as 1)

On platinum and metals of the platinum group, cyclohexane atoms can,

as follows from the sextet model of multiplet theory, be sorbed on the surface flat, losing six hydrogen atoms in the process. Upon desorption from the surface the molecule acquires six deuterium atoms and leaves into the bulk in the form of $C_6H_6D_6$. It is possible that, during its stay on the surface, the hydrogen atoms exchange places with deuterium atoms in such a way that, with rapid desorption, only some of the atoms have time to exchange, whereas with a longer one all six do. This may explain the presence of deuteration products with the number of deuterium atoms from one to five. The formation of products with seven or more deuterium atoms may be explained either by flipping over on the surface or by secondary adsorption of already deuterated cyclohexane.

Fig. 2. Dependence of the distribution of deuterocyclohexanes on time on Pt at 63° C; 1 –30 min after the start of exchange, 2 –after 60 min, 3 –after 180 min.

Anderson and Kemball reject the possibility of a sextet model on the grounds that on the same catalysts both cyclohexane and cyclopentane undergo exchange, while the latter, in their opinion, cannot react according to the sextet scheme. They indicate that it is more likely a matter of a doublet scheme. However, it should be noted that, according to B. A. Kazanskii, A. L. Liberman, and A. F. Platz ([8]), compounds of the cyclopentane series can react according to a doublet-sextet scheme, being superimposed by five atoms on a hexagon of platinum atoms in such a way that one of the C–C bonds in the cyclopentane molecule is deformed. We suppose that deuterium exchange in cyclopentane may also occur by a similar mechanism.

Exchange on iron and tungsten may proceed by a doublet scheme, in which the

Fig. 3. Distribution of deuterium-exchange products on W (at 163°) and Fe (at 124°).

Figure 3: Fig. 3. Distribution of deuterium-exchange products on W (at 163°) and Fe (at 124°).

presence of a noticeable peak at the sixth atom is not obligatory; exchange by a sextet-type mechanism cannot proceed on these metals, since the arrangement of atoms in the crystal lattice of these metals does not correspond to the structure of a six-membered ring. The possibility is not excluded that on platinum both types of mechanisms, doublet and sextet, are combined, and that depending on the conditions one of them predominates.

Fig. 3. Distribution of deuterium-exchange products on W (at 163°) and Fe (at 124°).

Thus, it may be supposed that one of the main factors determining the difference in the mechanism of the exchange reactions of cyclohexane on different catalysts is the crystalline structure of the metal.

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