MECHANISM OF TRANSFORMATION OF 1,3-DIOXACYCLOALKANES ON A PLATINUM CATALYST

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The paper reviews the experimental results relating to the mechanisms of the platinum-catalysed isomerization and hydrogenolysis of 1,3-dioxacycloalkanes, and the conclusions drawn from these. The formation of alkoxyoxo compounds as a result of isomerization can be attributed to active sites of an electrophilic character on the Pt/thermolite catalyst, and can be interpreted by an intramolecular mechanism.

Isomerization to the ester, configurational isomerization and hydrogenolysis are due to the platinum catalyst and the hydrogen chemisorbed on it, and the mechanisms of the processes are thus probably of an intermolecular character.

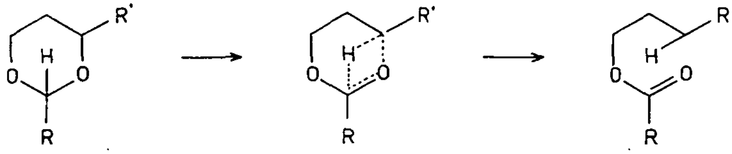
According to the results of our investigations performed so far in the field of the chemistry of the 1,3-dioxacycloalkanes, we have identified new heterogeneous catalytic isomerizations and certain characteristic features of their mechanisms.

Introduction

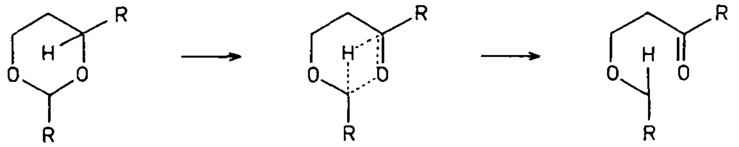
In the course of our experimental work it was proved in the case of many compounds (reviewed in [1]) that on a Pt/thermolite (Pt/T) catalyst in the presence of hydrogen, the five- and six-membered cyclic acetals undergo isomerization to esters with very good yields. The more surprising it is that the transformation is selective for the 1,3-dioxolanes, the less surprising the fact that isomerization accompanied by ester formation does not take place in the case of the 1,3-dioxepanes and the 1,3-dioxocanes from the homologous series of cyclic acetals, isomerization involving opening of the C_2-O bond occurring instead, together with hydrogenolysis. Ester formation cannot be observed under similar conditions in the transformation of open chain acetals either.

In the liquid phase, under conditions suitable for radical reactions (UV light, presence of peroxides), the five- and six-membered cyclic acetals, and the open-chain acetals, too, undergo transformations accompanied by the formation of esters [2—9], but the selectivity is substantially poorer than that in heterogeneous catalytic isomerization. It was assumed earlier that under similar conditions the 1,3-dioxepanes, too, can be induced to undergo analogous transformations. From this aspect our examinations proved unavailing, for under similar conditions the 1,3-dioxepanes polymerized. Publications can also be found relating to the vapour-phase thermal isomerization of 1,3-dioxanes, where the formation of esters is reported [10—12]. Although the C_4-O and C_6-O bonds are conjugated with double bonds (allyl-type conjugation) in some of the listed cases, nevertheless the authors discussing the mechanism of the reaction state without exception that the initial step in the reaction is the radical-type loss of hydrogen from C_2. In the final analysis, the non-occurrence of isomerization to the ester in the case of the 1,3-dioxepanes, the 1,3-dioxocanes and the open-chain acetals on Pt/T may bear witness to the fact that the structure of the substrate determines the direction of the processes taking place within one compound type.

If an intramolecular character is attributed to both types of isomerizational transformation of 1,3-dioxacycloalkanes on Pt/T, the two processes can be regarded as 1,3-hydrogen migration, and can be formally interpreted according to the doublet mechanism of the multiplet theory [13]. In the case of ester formation, the H atom is transferred from C_2 to C_4 *via* a four-membered transition state:



In the case of the formation of alkoxyoxo compounds the direction of hydrogen atom transfer is the reverse of the above:



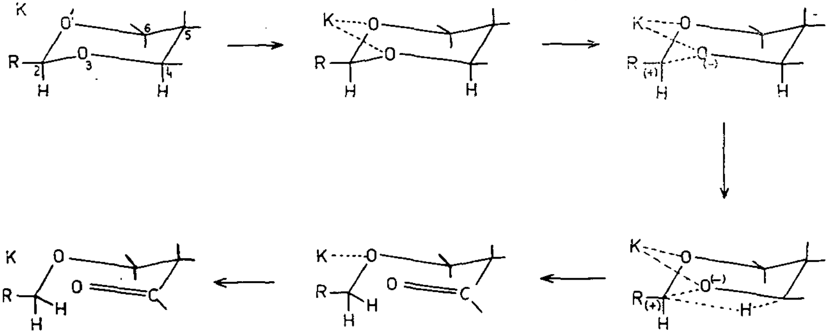
On this basis, *i.e.* considering the changes only formally, in the classification scheme of BALANDIN [13] the two processes can be listed among reactions with the index $\mathrm{II}\,\mathrm{K}^{3}_{17}{}^{\mathrm{CO}}_{\mathrm{HC}}$.

However, our experimental observations to date indicate that the two isomerization processes do not take place by mechanisms of similar type: the formation of the alkoxyoxo compounds is very probably of an intramolecular character, whereas the formation of the esters seems to be a process with an intermolecular mechanism.

Only comparative data of a qualitative nature are available concerning the thermodynamic driving force of the process (the stability of the corresponding esters, but mainly of the cyclic acetals). These data show that, in their thermal decompositions and heterogeneous catalytic transformations, the esters exhibit higher stability than the cyclic acetals [14]. Thus, it may be assumed that in their heterogeneous catalytic transformations the formation of the transition complex necessary for the isomerization of the otherwise reactive 1,3-dioxepanes and 1,3-dioxocanes to esters is prevented by adsorption inhibitions decisively not attributable to energetic reasons, but to reasons closely related with the stereostructures of the rings, *i.e.* to geometric reasons. As regards the mechanisms of the processes observed in the transformation of 1,3-dioxacycloalkanes, further complex experiments are required. The large amount of hydrogen chemisorbed on the surface of the platinum can take part in complex surface transformations, and in our view it is this circumstance which determines the mechanisms of the processes in most cases. Thus, on Pt/T and Pt/C in helium atmosphere isomerization to the ester does not occur, and other, non-catalytic, but mainly pyrolytic processes are observed.

Mechanism of the formation of alkoxyoxo compounds

In the course of the investigations on the transformations of 1,3-dioxanes, 1,3-dioxepanes and 1,3-dioxocanes on platinum catalysts, the formation of alkoxyoxo compounds was observed in the case of the acetals and the ketals. Although a number of solutions are possible in principle with regard to the mechanism of the process, the formation of the alkoxyoxo compounds can be interpreted in accordance with the Rondestvedt mechanism [16], reported in detail previously [15]. On the basis of our experimental data, therefore, the formation of the alkoxyoxo compounds must be attributed to active sites of an electrophilic character on the Pt/T catalyst, and may thus be interpreted by means of 1,3-hydride anion migration according to an intramolecular mechanism:

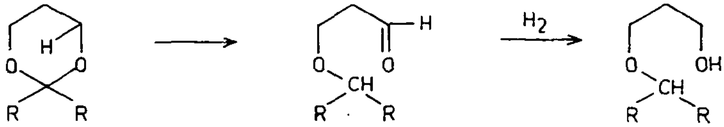


From the results to date of investigations on individual diol monoethers and alkoxyoxo compounds, under the same experimental conditions as for the corresponding dioxacycloalkanes, it may be concluded that two processes accompanied by splitting of the C_2-O bond take place in parallel: namely the formation of alkoxyoxo compounds and the formation of diol monoethers. Otherwise, the primary process character of the isomerizational transformation accompanied by formation of the alkoxyoxo compounds is proved by the fact that it can also be observed at a comparatively low temperature, when the dehydrogenation of the diol monoethers does not yet proceed. Its intramolecular character is proved by the facts that it also takes place in the absence of hydrogen, and that the presence of ammonia inhibits the isomerization, in contrast to the other two main processes (hydrogenolysis, ester formation). At the same time, these latter experimental data indicate that the occurrence of this isomerizational change can be attributed to active sites of an electrophilic character on the Pt/T. Further it should be noted that on Pt/C the isomerization of 1,3-dioxanes to β-alkoxyoxo compounds cannot be observed, which similarly supports the above conclusions.

Hydrogenolysis of 1,3-dioxacycloalkanes

In the course of our experimental work it was found that under the experimental conditions applied in the impulse technique, the acetal-type derivatives of the seven- and eight-membered 1,3-dioxacycloalkanes, and also the six-membered cyclic ketals, very readily undergo splitting on the action of hydrogen in the presence of Pt/T.

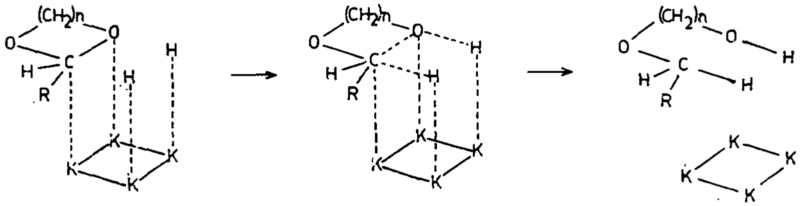
It is understandable that an intermolecular and unconditionally primary character must be attributed to the process of hydrogenolysis, although in principle the formation of the diol monoethers can also be explained by means of consecutive processes: the hydrogenation of the alkoxyoxo compounds formed as intermediates:



However, it is necessary to take into consideration the above statements indicating the parallel nature of the two processes, and that in certain cases the hydrogenolysis proceeds also at low temperatures at which isomerization accompanied by formation of the alkoxyoxo compounds is not observed at all; the primary nature of the hydrogenolysis involving formation of the diol monoethers is then clear-cut.

The high rate of the hydrogenolysis points to a low activation energy (calculated from our experimental results as ~4 kcal/mole), in contrast to the isomerization processes accompanied by splitting of the C-H bonds, which have a significantly higher activation energy (18—20 kcal/mole), and therefore they proceed optimally at higher temperatures.

Of the hypotheses relating to the mechanism of the hydrogenolysis, those assuming one- or two-point adsorption of a substrate molecule with simultaneous or consecutive uptake of the two chemisorbed hydrogen atoms can be regarded as most probable. One of the possibilities is illustrated in the following scheme:



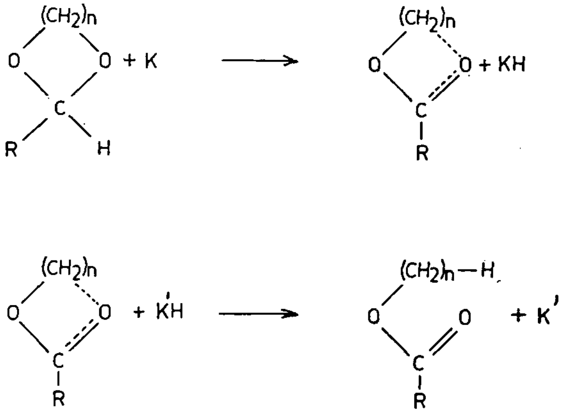
Mechanism of isomerization of the 1,3-dioxacycloalkanes to esters

Our experimental data show that of the 1,3-dioxacycloalkanes on Pt/T in the presence of hydrogen, mainly the five- and six-membered acetals are isomerized readily to esters, the stereostructures of which permit the adsorption of the "entire ring". The envelope or half-chair conformation of the 1,3-dioxolanes and the chair conformation of the 1,3-dioxanes each allow the carbon atoms (as the centres affected in the reaction) adjacent to the oxygen atoms to arrange themselves (in a plane parallel to the imaginary plane of the catalyst in adsorption with a preferred direction). In the case of the above conformations the C_2-H, C_4-H and C_6-H atoms have axial orientations. This state permits dissociative chemisorption of the C_2-H bond, which in our view is the condition for ester formation. The ready, flexible deformation of the six-membered ring systems with distorted conformations, and also of the seven- and eight-membered ring systems, does not favour the development of the adsorption state with the above-mentioned fixed structure, with the consequence that the ester is not formed.

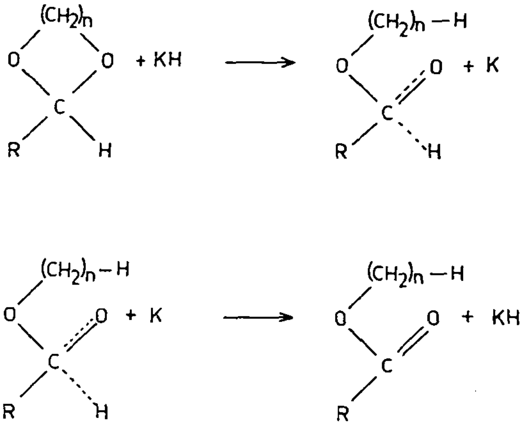
An experimental fact worth of note in the interpretation of the stereochemistry of the transformations is that, in *trans*-1,3-dioxadecalin, *i.e.* in the case of equatorial C-O annellation, the ester formation is an inhibited process.

It has already been mentioned that the mechanism of the ester formation process differs fundamentally from the mechanism of isomerization of the dioxanes involving the formation of alkoxyoxo compounds; an intramolecular character has been attributed to the latter mechanism on the basis of our experimental data obtained so far. The difference can be seen in the fact that the two isomerization processes react in different ways to the same external effect: in a carrier gas stream of helium the ester formation process does not take place, and it is not inhibited by the presence of ammonia; it similarly takes place on other catalysts capable of chemisorbing hydrogen, such as Rh/T, but on Cu/Al there is no ester formation. Therefore, according to our experimental data, isomerization to the ester is achieved with the participation of hydrogen sorbed on the catalyst. Several reaction schemes can be written for this; two essentially different possibilities are given below.

The process starting with splitting of the C_2-H bond comes to an end with the binding of the sorbed hydrogen to C_4, which results in the formation of the corresponding ester:



Alternatively, the hydrogen sorbed on the catalyst opens the ring at C_4, the transition state produced being stabilized in the process of ester formation by the splitting off the hydrogen from C_2:



The detailed study of the validity of the two mechanisms outlined is now in course, with the application of isotope tracer techniques and IR examinations.

As regards the adsorption of the substrate molecules, it must be unfavourable for hydrogenolysis, *i.e.* the oxygen atoms may not be near the surface of the catalyst. In the absence of kinetic data it naturally cannot be said what part-processes or what step of the transformation can be regarded as rate-determining, but it can be seen that the direction of the transformations is significantly affected by the stereostructure of the molecule of a cyclic acetal, and by the spatial arrangement of the substituents. The non-occurrence of isomerization in the dioxepanes, the considerable difference between the reactivities of the stereoisomeric dioxadecalins, and the behaviour of stereoisomers with different conformations, clearly prove the role of the steric factors.

As regards the reactivity of the 1,3-dioxacycloalkanes it is necessary to single out the substituents on C_2 and C_4, since these act directly on the C-O and C-H bonds undergoing splitting in the transformation, the bond strengths of which play an important role in the directions and rates of the transformations. In the case of formals the H atoms on C_2 are less mobile, and consequently less reactive. The alkyl groups on C_2 promote the transformation of the dioxanes in the sequence of their positive inductive effects. However, the substituents promote the splitting of the C_2-H bond and accordingly the isomerization to the ester not only by weakening the strength of the C_2-H bond, but also by means of their effect on the direction of adsoprtion of the molecule. The effects of the substituents at C_4 on the rates and directions of transformation of the dioxanes can be interpreted in a similar way. The reason is that the substituents on C_4 affect the strength of the C_4-O_3 bond. Consequently, the rate of formation of the esters of primary alcohols in the transformation of 4-monosubstituted 1,3-dioxanes is higher than that of the formation of the esters of secondary alcohols produced by splitting of the C_6-O_1 bond.

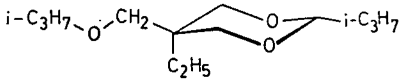
The fastest transformation is that of cyclic acetals containing the C_2-phenyl group; this follows from the special structural features of the molecule (the aromatic ring is in conjugation with the C_2-O bond), and from the capability of the phenyl group for adsorption. Thus, the presence of the phenyl group can result in transition states with structures which favour the splitting of the C_2-O bond, and hence the formation of the corresponding diol monoether and the alkoxyoxo compound. It is possible to interpret in a similar way the rate-increasing effect of the phenyl group at C_4 as regards ester formation.

The determining role of the substituents is best illustrated by the reaction rate sequence, formal$<$acetal$\ll$ketal, observed in the case of the 1,3-dioxanes, and also the various reaction direction affecting this sequence.

Although the studies with stereoisomers of different conformations are still in the initial stage, since establishment of the mechanisms of the processes occurring on the action of the catalysts requires the solution of many part-problems, we consider that even the results available up to now permit a clear interpretation of the processes involved.

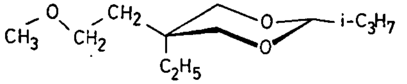
The interpretation of the transformation of 1,3-dioxacycloalkanes on Pt/T in the presence of hydrogen requires the establishment of the most fundamental factors which affect the course of the two parallel main processes, the hydrogenolysis and the isomerization to esters.

The causes for the two main reactions to occur which can be ascribed to the structure of the molecule can be seen quite clearly in model compounds I and II, for instance:



I

hydrogenolysis

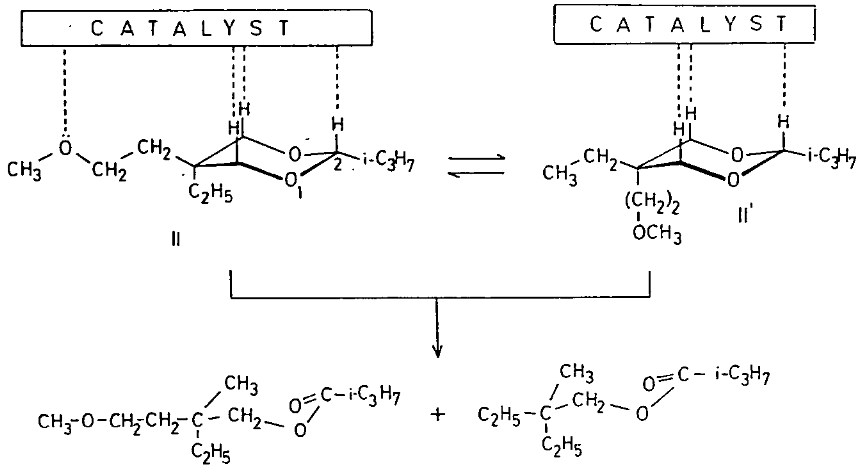


II

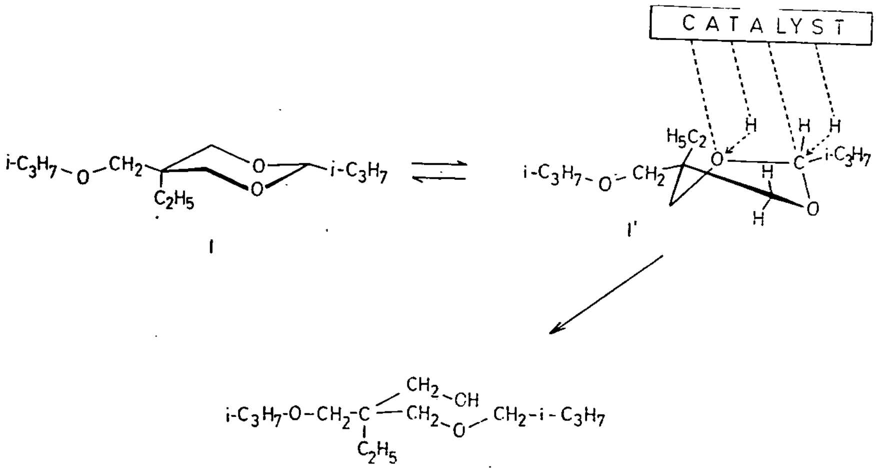
isomerization

The experimental data obtained on approximately identical Pt/T catalysts in a carrier gas stream of hydrogen show that hydrogenolysis proceeds with great selectivity in the case of I, and ester formation in the case of II. In our view, the different behaviours can be attributed to the fact that, as a result of their different stereostructures, the two molecules are chemisorbed in different geometrical arrangements on the surface of the catalyst.

II may be bonded to the surface along the axial hydrogens of the dioxane ring. This arrangement of the molecule may be promoted by the 5β-alkoxy group (by means of the non-bonded electron-pair of the oxygen atom). Adsorption of the molecule in such a situation decreases the probability of hydrogenolysis by keeping the C_2, O_1 and O_3 atoms of the dioxane ring away from the surface of the catalyst. At the same time, isomerization to the ester is promoted by means of splitting of C_2-H bond. The above-mentioned oriented adsorption of II is strongly suggested not only by the ester formation, but also by the experimental fact that in the case of compounds containing the equatorial 5β-alkoxy group, in contrast to compounds containing the 5α-alkoxy substituent, it was also possible to observe the formation of products involving hydrogenolysis of the β-alkoxy group:

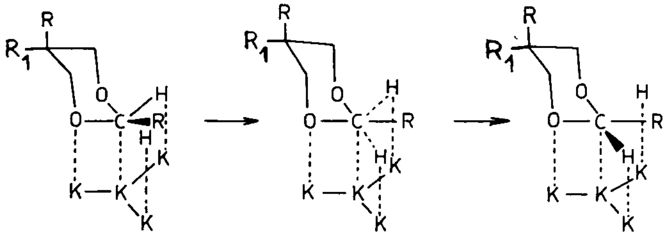


The adsorption of molecule I in a similar way to that of II can be hindered by two factors: *(i)* its configurational isomerization to the asymmetric isomer with the twisted boat conformation (which, on the basis of our experiments and in the knowledge of the main reaction kinetic parameters of transformations of a similar character observed in the case of alicyclic hydrocarbons [17], is a very fast process), and *(ii)* the absence of the surface-fixing effect of the *trans* side-chain. The molecule probably undergoes adsorption along the C_2-O bond, a consequence of which is the hydrogenolysis of the molecule:



Interpretation of the configurational isomerization

Prior to the commencement of our investigations, we found no literature data describing the configurational isomerization of the 1,3-dioxacycloalkanes. Recently, however, two research groups (ELIEL *et al.* [18] and BOGATSKII *et al.* [19]) reported that the 1,3-dioxanes undergo configurational isomerization in the presence of electrophilic catalysts. In the present case the transformation was induced under substantially different conditions, *viz.* on the action of Pt/T. In the process of configurational isomerization the determining role must similarly be attributed to the chemisorbed hydrogen; for under otherwise similar experimental conditions, but in the absence of hydrogen, the occurrence of this isomerizational change cannot be observed. The appearance of isomerization can be ascribed to the configurational change occurring at C_2 on the action of hydrogen, and thus can be interpreted similarly as for S_N2 reactions. Of course, in the process of isomerization the tetrahedral orientation of C_2 is deformed.



This mechanism is supported by the relatively low activation energy of the process (6—8 kcal/mole).

The isomerization in the opposite direction, *i.e.* the isomerization of the asymmetric stereoisomer with the twisted boat conformation, proceeds in an analogous manner. In the long run equilibrium might be established between the two stereoisomers if this were not affected by other, consecutive processes (in this case, isomerization to the ester, or hydrogenolysis).

Understandably, the mechanism of the isomerization process *cis*-1,3-dioxadecalin→*trans*-1,3-dioxadecalin differs essentially from the above, since a change takes place also in the annellation of the two six-membered rings. The different nature of the isomerization is revealed by the fact that, in contrast to the above, the opposite process, *i.e.* the transformation of *trans*-2-methyl-1,3-dioxadecalin to some *cis* isomer, could not be observed. Later investigations in this field must aim at the separation of further stereoisomers, and at the examination of the transformations of these stereoisomers on Pt/T. Study of the above-outlined mechanism of the configurational isomerization is also justified, for adsorption on several points of the substrate molecule is not unconditionally necessary for the occurrence of isomerization.

The experimental results observed so far in connection with 1,3-dioxacycloalkanes on Pt/T are summarized below.

The reaction directions determined by the structures of the compounds and by the experimental conditions have been recognized to be effected by the main parameters. The formation of alkoxyoxo compounds is attributed to active sites of an electrophilic character on the Pt/T, and interpreted by an intramolecular mechanism.

The roles of the platinum catalyst and the hydrogen on it are confirmed by the occurrence of hydrogenolysis, ester formation and configurational isomerization, and thus the mechanisms of the processes are probably of an intermolecular character.

Several factors resulting from the structures of the substrate molecules and affecting the main processes have been discerned, *e.g.* the number of ring atoms, the nature, number, position and configuration of the substituents, the direction of adsorption on the substrate molecule, the bond strengths of the bonds of the substrate molecule, etc. In order to understand the details of the mechanism, it is necessary to carry out complex examinations of the system catalyst — hydrogen — substrate by various methods [20].

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МЕХАНИЗМ ПРЕВРАЩЕНИЙ 1,3-ДИОКСАЦИКЛОАЛКАНОВ В ПРИСУТСТВИИ ПЛАТИНОВОГО КАТАЛИЗАТОРА

М. Барток, Й. Апьок

В сообщении подводятся итоги изучения механизма изомеризации и гидрогенолиза 1,3-диоксациклоалканов с обсуждением экспериментальных результатов.

Образование алкокси-оксосоединений при изомеризации 1,3-диоксациклоалканов можно истолковывать по механизму внутримолекулярного характера, посредством электрофильных центров катализатора Pt/T. Изомеризация в сложные эфиры, конфигурационная изомеризация и гидрогенолиз происходят только в присутствии хемосорбированного водорода, следовательно, механизм этих процессов носит межмолекулярный характер.