# ORGANIC CHEMISTRY

EFFECT OF HYDROGEN PARTIAL PRESSURE ON CATALYTIC TRANSFORMATIONS OF  $C_6$  ALKANES AND METHYLCYCLOPENTANE ON Pt/C

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Hydrogen has an important effect on the rate and selectivity of a number of catalytic reactions on metal-containing catalysts. The presence of hydrogen in the reaction zone is a necessary condition for the  $C_5$ -dehydrocyclization ( $C_5$ -DHC) and isomerization of alkanes on Pt catalysts [1-3]. The role of hydrogen in the mentioned reactions is paramount, al-though the dispersity of the metal particles and the nature of the support also have importance [4].

In the present paper we studied the effect of the  $H_2$  partial pressure in its mixtures with He on the rate and selectivity of the reactions for the  $C_5$ -cyclization and skeletal isomerization of  $C_6$  alkanes and olefins, and also for the hydrogenolysis of methylcyclopentane and 1-methylcyclopentane on Pt/C catalyst. Since the reactions for the  $C_5$ -DHC of alkanes and the hydrogenolysis of alkylcyclopentanes are reversible, while the reaction for the skeletal isomerization of alkanes is intimately related to them [5], a common examination of these mutual transformations represents a necessary and important step in ascertaining the mechanism of the effect of hydrogen during the progress of the indicated reactions.

## EXPERIMENTAL

The 20% Pt/C catalyst was prepared as described in [6]. The surface area of the metal phase, calculated from the x-ray structure data, was equal to  $31 \text{ m}^2/\text{g}$ .

n-Hexane  $(n-C_6)$ , 3-methylpentane (3-MP), 2,2-dimethylbutane (DMB), methylcyclopentane (MCP), 3-methyl-2-pentene (3-MP-2), and methyl-1-cyclopentene (MCP-1) were purified on highly efficient rectification columns to a purity of at least 99.5%.

The experiments were run in pulse microcatalytic equipment (Fig. 1) in a stream of H2, He, and their mixtures (3 liters/h, 1 gauge atm) on Pt/C (0.037 g) at 280 and 310°C. The hydrocarbon sample (1.5  $\mu$ l) on exit from reactor 6 was condensed in trap 8, cooled with liquid nitrogen, and, using a stopcock metering device, was routed to the analytical section of the equipment. The use of separate gas streams in the reaction and analytical sections of the equipment made it possible to exclude the effect of changes in the reaction conditions on the GLC analysis. Prior to each pulse the catalyst was heated in a stream of the appropriate gas mixture for 40 min at the reaction temperature. The activity of the catalyst dropped rapidly in an He stream and when the H<sub>2</sub> content in the gas mixture was below 20%. In this case the catalyst was activated by a pulse of 5 ml of air and then was heated in a stream of the appropriate gas mixture for 40 min. The constancy of the catalyst activity was checked periodically under standard conditions (310°, 100% H<sub>2</sub>). The analysis was run on two parallel capillary columns (50 m) packed with triethylene glycol dibutyrate at 20°, which were preceded by a tube filled with 10% Pd/SiO2, heated to 110°, for hydrogenating the unsaturated compounds in the catalyzate. The gas mixture was analyzed prior to each pulse on a column  $(18 \text{ m} \times 0.3 \text{ cm})$  packed with 5-Å molecular sieves at 20°.

## DISCUSSION OF RESULTS

The composition of the catalyzates, obtained in the transformations of  $n-C_6$ , 3-MP, and MCP on Pt/C at 310°, in the experiments with a variable amount of hydrogen in the gas mixture, is given in Table 1.

\*Deceased.

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TABLE	1
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	He concend		Catalyzate composition The						
Hydro- carbon	tration,	C,C5	DMB	2-MP	3-MP	n-C <sub>6</sub>	MCP	olefins*	$C_6H_6$
3 -MP	100 55 41 26 15 5 0	2,3 2,9 1,4 2,6 3,0 1,1 0,1	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	7,8 13,7 12,0 9,6 7,5 3,1 -	87,2 77,8 79,6 81,7 81,0 89,0 96,0	2,13,74,93,13,71,2-	0,4 1,7 1,7 2,5 4,2 5,3 0,1		- 0,1 0,2 0,4 0,2 0,1
n-C6	$     \begin{array}{r}       100 \\       57 \\       41 \\       26 \\       4 \\       0     \end{array} $	1,3 2,2 1,8 3,2 1,5 0,1	-	2,6 5,8 7,6 7,8 1,0 -	$ \begin{array}{c} 1,1\\2,8\\3,3\\3,9\\0,8\\-\end{array} $	94,3 87,6 84,4 81,1 89,5 94,4	0,6 1,1 1,7 2,3 4,0 -	 	0,1 0,5 1,1 1,7 2,2 1,6
МСР	$     \begin{array}{r}             100 \\             57 \\             42 \\             27 \\             3 \\             0         \end{array}     $	$0,6 \\ 0,6 \\ 1,3 \\ 2,0 \\ 0,2$	-	$\begin{array}{c c} 31,1 \\ 26,1 \\ 25,4 \\ 21,5 \\ 0,8 \\ - \end{array}$	12,3 10,4 13,0 12,2 0,7	$     \begin{array}{r}       6,9 \\       4,9 \\       6,3 \\       6,1 \\       0,3 \\      \end{array} $	49,1 57,9 53,8 57,9 93,1 96,4	- - - 4,7/- 3,4/-	0,1 0,1 0,3 0,2 0,1

\*Cyclic olefins/acyclic olefins.



Fig. 1. Diagram of pulse equipment: 1) P-280 pressure reducer; 2) RG-17 regulator of gas flow; 3) gas purification; 4) addition of sample; 5) katharometer; 6) reactor; 7) stopcock metering device; 8) loop for condensing hydrocarbon pulse; 9) metal tube filled with  $Pd/SiO_2$ ; 10) capillary column; 11) flame-ionization detector.

The data plotted in Fig. 2 illustrate the direct effect of the  $H_2$  in the carrier gas on the rate for the  $C_5$ -DHC of alkanes and  $C_5$ -cyclization of alkenes. The curves for the yield of MCP from  $n-C_6$ , 3-MP, and 3-MP-2 pass through a maximum in the region of a relatively low  $H_2$  content. The similarity in the character of the curves makes their common discussion possible. In harmony with the results in [3, 4], the left ascending portion of the curves demonstrates that in the presence of Pt/C the presence of  $H_2$  is a necessary reaction condition for the formation of a five-membered ring from alkanes and olefins. The descending branch indicates the substantial slowing up of the cyclization rate with increase in the  $H_2$ The latter was already observed by us under other conditions [3] and apparently content. has several reasons. Two of them seem to be the most important: first, hydrogenolysis of the five-membered ring, which proceeds vigorously in excess H2 (see Table 1), and second, the inhibiting effect of H2, discussed in a number of papers, on the transformations of hydrocarbons during H<sub>2</sub> adsorption on the surface of metal catalysts. This phenomenon is apparently caused by a decrease in the amount of free surface due to filling by hydrogen and, as a consequence, suppression of the chemisorption of hydrocarbons [7].

The group of curves in Fig. 3 reflects the results of studying the skeletal isomerization of alkanes and 3-MP-2. The isomerization is intimately related to the formation and hydrogenolysis of a five-membered ring [5]. The results obtained in the presence of Pt/C (see Fig. 3) are qualitatively in good agreement with the data given in [1, 8] on Pt black. However, Pt/C exhibits certain traits as an isomerization catalyst, namely the C<sub>5</sub>-DHC of



Fig. 2. Yield of cyclization products of 3-methylpentane (1), n-hexane (2), and 3-methyl-2-pentene (3) as a function of  $H_2$  content in carrier gas at 280 (a) and 310° (b).

Fig. 3. Total yield of skeletal isomerization products of 3methylpentane (1, 5), 3-methyl-2-pentene (2), n-hexane (3, 6), and 2,2-dimethylbutane (4) as a function of  $H_2$  content in carrier gas (1-4 at 310°; 5, 6 at 280°).

alkanes. In contrast to the reactions for the formation of  $C_5$ -rings from alkanes and olefins, the skeletal isomerization of alkanes, and also of olefins, proceeds at the fastest rate in the region of medium H<sub>2</sub> concentrations. The isomerization curves have much more diffuse maxima than in the case of  $C_5$ -DHC (cf. Figs. 2 and 3). In the absence of H<sub>2</sub>, the skeletal isomerization of alkanes practically does not go on Pt/C. A comparison of the results, obtained in the isomerization of normal (n-C<sub>6</sub>) and iso (3-MP, DMB) hydrocarbons, reveals that, in contrast to  $C_5$ -DHC, the maxima in the case of the starting n-C<sub>6</sub> are found in the region of a relatively lower H<sub>2</sub> partial pressure. These facts could be due not only to the amount of H<sub>2</sub> in the gas mixture, but also to the energy nonequivalence of the adsorbed



hydrogen forms, needed for the isomerization and  $C_5$ -DHC of alkanes. In particular, the possible involvement of firmly adsorbed hydrogen in the  $C_5$ -DHC reaction, and of weakly adsorbed forms in the isomerization of alkanes, was mentioned by us in [3]. Besides the existence of various types of hydrogen, chemisorbed on Pt, it is also necessary to take into account the different functions performed by hydrogen on the surface of metal catalysts [7]. As a result, the positions of the maxima in Fig. 3, the same as during  $C_5$ -DHC, depend on the effect of H<sub>2</sub> of variable character. When the temperature is lowered there is a tendency to shift the region of the maxima toward a lower H<sub>2</sub> content in the gas, which is apparently related to an increase in the degree of filling the catalyst surface by active hydrogen. A similar character of the relationships, obtained in the transformations of 3-MP and 3-MP-2 (see Figs. 2 and 3), indicates that the hydrogenation step apparently precedes the reactions for the C<sub>5</sub>-cyclization and isomerization of olefins.

The isomerization of DMB deserves special attention (see Fig. 3). The structure of DMB excludes its isomerization by the cyclic mechanism [5].\* Consequently, it would seem that the skeletal isomerization of DMB should proceed predominantly by the mechanism of bond shifts [9], i.e., in the region of a relatively low surface concentration of hydrogen [4].

\*Actually, only traces of MCP were observed in the DMB catalyzates.



Fig. 4. Total yield of hydrogenolysis products of methylcyclopentane (1,  $310^{\circ}$ ; 2,  $280^{\circ}$ ) and methylcyclopentene-1 (3,  $310^{\circ}$ ) as a function of H<sub>2</sub> content in carrier gas.

Fig. 5. Selectivity of forming isomeric hexanes from 3methylpentane (1), 3-methyl-2-pentene (2), n-hexane (3), methylcyclopentane (4), and methyl-1-cyclopentene (5) as a function of  $H_2$  content in carrier gas at 310°.

At the same time, the maximum on the curve for the isomerization of DMB actually coincides with the maximum in the case of 3-MP. This apparent contradiction is difficult to explain if we do not take into account the fact that an important factor, affecting the character of the obtained curves and the form of the maxima, is the degree of filling the active surface of the catalyst by hydrogen. However, we will mention that the mechanism of bond shifts is not always sensitive to differences in the  $H_2$  content; thus, in [8] small amounts of DMB are formed from 3-MP in a wide range of  $H_2$ -He concentrations.

The active hydrogen concentration on the catalyst surface differs under the conditions of the various reactions. Apparently, this is specifically the reason for the different position of the maxima in the various reactions and even in the case of different hydrocarbons. This effect is observed even more clearly when using different Pt catalysts [4]. Also taking into account the fact that the structure of the acting catalyst, and also its activity and selectivity, change during reaction under the influence of the reaction medium (in our case the hydrocarbon and H<sub>2</sub>), it becomes evident that the selectivity of the Pt/C action can be regulated quite broadly by varying the H<sub>2</sub> partial pressure. A direct determination of the true surface concentration of hydrogen under the reaction conditions does not seem possible as yet. Consequently, the data on the progress of various reactions under identical conditions assume special importance, as well as information on the selectivity of the previous conclusions on the important role of the real filling of the active surface of the catalyst by hydrogen during the C<sub>3</sub>-DHC of alkanes [10] and the hydrogenolysis of alkylcyclopentanes [11] in the presence of Pt/C.

In Fig. 4 and Table 1 are given the data on the hydrogenolysis of MCP and MCP-1 along directions 1-3. A similar character of the curves is observed during the hydrogenolysis of



MCP and MCP-1 along the indicated directions, which indicates a monotonic increase (up to a certain limit) in the hydrogenolysis rate of both hydrocarbons, with a probable prior hydrogenation of MCP-1 to MCP. The appearance of a maximum on the curve for the hydrogenolysis of MCP when the temperature is lowered can be caused for the same reasons as in the case of the reactions for the  $C_5$ -dehydrocyclization and isomerization of alkanes.

The selectivity of forming the isomeric hexanes from various  $C_6$  hydrocarbons permits making more complete judgment regarding the mechanisms of their transformations. In Fig. 5 are plotted the ratios of the 2-MP/n-C<sub>6</sub> and 2-MP/3-MP concentrations, which are formed as the result of the respective catalytic transformations of 3-MP, 3-MP-2, MCP, MCP-1, and also n-C<sub>6</sub>, MCP, and MCP-1. The fact that the indicated ratios practically coincide in the case of isomerization and hydrogenolysis is convincing proof for the predominant contribution made by the C<sub>5</sub>-cyclic mechanism in the process for the skeletal isomerization of 3-MP and n-C<sub>6</sub>. It should be emphasized that a complete coinciding of the indicated ratios in the entire range of H<sub>2</sub>-He concentrations, especially in the region of low hydrogen concentrations, is characteristic for Pt/C. Consequently, even under conditions that are more preferable for the mechanism of bond shifts, the contribution of the C<sub>5</sub>-cyclic mechanism on Pt/C is quite large. In this respect Pt/C is noticeably different from Pt black [1, 4]. This is possibly due to the effect of the larger size of the crystallites in the case of Pt black, which is in agreement with the data in [12], on which basis was predicted the greater contribution of the mechanism of bond shifts on Pt catalysts with large crystallites.

The formation of benzene from n-C<sub>6</sub> is noticeably manifested both in the absence and with a relative deficiency of H<sub>2</sub>, and is suppressed when the amount of H<sub>2</sub> is increased (see Table 1). The obtained data differ from the corresponding results plotted in Figs. 2 and 3: the amount of olefins and benzene in the catalyzate decreases with increase in the H<sub>2</sub> concentration. The progress of C<sub>6</sub>-DHC in a He medium and the different effect of hydrogen (especially in the region of low concentrations) on the C<sub>5</sub>-DHC-isomerization of alkanes and on C<sub>6</sub>-DHC of alkanes [13, 14]. Hydrogen is necessary for the C<sub>5</sub>-DHC of alkanes, which, in harmony with [2, 15], enters into the composition of the associative transition state that is adsorbed on the catalyst surface. However, we will mention that the position of the maxima on the curves (see Fig. 2) in the region of a relatively low H<sub>2</sub> concentration also indirectly indicates another possibility for progress of the reaction, namely via the intermediate formation of unsaturated compounds. The reality of such a path for the C<sub>5</sub>-DHC of alkanes on Pt/C was shown previously in [16].

As a result, the obtained data testify to the direct effect of the H<sub>2</sub> partial pressure on the rate and selectivity of the transformations of hydrocarbons in the presence of Pt/C. The most important is the result on the selectivity of the skeletal isomerization of aliphatic hydrocarbons and the hydrogenolysis of cyclic hydrocarbons. The obtained data confirm the decisive contribution of the cyclic mechanism in the isomerization-C<sub>5</sub>-DHC of alkanes in a wide range of H<sub>2</sub>-He concentrations. The important role of the surface concentrations of hydrogen was shown for the progress of the C<sub>5</sub>-DHC and skeletal isomerization reactions of alkanes, the hydrogenolysis of MCP, and also the C<sub>6</sub>-DHC of n-C<sub>6</sub> in the presence of Pt/C. The obtained results are in good agreement with the data that postulate differences in the mechanisms of the C<sub>5</sub>- and C<sub>6</sub>-DHC of alkanes. At the same time, these results do not exclude the possible partial progress of the C<sub>5</sub>-DHC of alkanes by the dissociative path with the formation of intermediate unsaturated compounds.

#### CONCLUSIONS

1. The regions of the optimum amount of hydrogen in  $H_2$ -He mixtures during the progress of the reactions for the C<sub>5</sub>-dehydrocyclization (C<sub>5</sub>-DHC), isomerization, and aromatization of C<sub>6</sub> alkanes, and also the hydrogenolysis of methylcyclopentane on Pt/C catalyst, were ascertained.

2. The obtained results testify to the fact that the presence of hydrogen is a necessary condition for the progress of the  $C_s$ -DHC-isomerization reactions of alkanes (olefins) on Pt/C catalyst, and indicate the important role of the surface concentration of hydrogen under the conditions of running the reaction.

3. The obtained data speak in support of the  $C_5$ -cyclic mechanism for the isomerization of alkanes in the presence of Pt/C catalyst.

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EFFECT OF HYDROGEN REMOVAL THROUGH A MEMBRANE CATALYST

ON DEHYDROCYCLIZATION OF n-HEXANE

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The dehydrocyclization of n-hexane (NH) has been accomplished on unsupported Pd catalysts, and specifically on Pd ribbon [1] and foil made from Pd-Ni alloy [2]. The dehydrocyclization of NH on a membrane catalyst (MC), pervious only to  $H_2$ , was studied in the present paper.

### EXPERIMENTAL

As the catalyst we used a spiral tube made from Pd alloy containing 5.89% of Ni, with an outside diameter of 2.5 mm, a length of 1 m, and a wall thickness of 0.1 mm. The prior treatment of the catalyst was described in [3]. The tube was contained in a steel cylinder and was washed on the outside with the vapors of a chromatographically pure NH-Ar mixture, which was fed from two thermostatted spargers. A part of the H<sub>2</sub>, liberated during the dehydrocyclization of NH, diffused through the tube walls and was removed by the Ar fed inside the tube. After each experiment, which lasted 1 h, the catalyst was regenerated at  $580^{\circ}$ C, at first with air (1 h) and then with H<sub>2</sub> (1 h). While cooling to the experiment temperature and between experiments the catalyst was found in an Ar atmosphere.

The liquid reaction products were analyzed on a Tswett 1-64 chromatograph, equipped with a  $2 \text{ m} \times 4 \text{ mm}$  column packed with 5% Benton-34 and 12% dodecyl phthalate deposited on Chromosorb P. The gaseous products were analyzed on a  $3 \text{ m} \times 3 \text{ mm}$  column packed with Al<sub>2</sub>O<sub>3</sub>.

## DISCUSSION OF RESULTS

The amount of benzene in the transformation products of NH on the given MC, at an Ar (carrier gas) flow rate of 13 ml/min and an NH partial pressure of 45 torr, increases up to 66 mole % when the temperature is raised to 515°. The dehydrocyclization is not accompanied by the formation of either methylcyclopentane or hexenes. Below 520° only H<sub>2</sub> was found in the gaseous products, and hundredths of a percent of ethane and ethylene at higher temperatures.

The H<sub>2</sub> partial pressure in the NH dehydrocyclization zone was decreased by increasing the rate of removing the formed H<sub>2</sub> through the MC. An increase in the Ar flow rate in the H<sub>2</sub> removal zone lowered the H<sub>2</sub> concentration in the dehydrocyclization zone.

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