DEPENDENCE OF THE DIRECTIONS OF CATALYTIC DEMETHYLATION OF 2-METHYLHEXANE ON ITS ELECTRONIC STRUCTURE

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UDC 541.128:547.216

In our studies [1, 2] it was shown that an increase in the pressure of H_2 promotes hydrogenolysis of the bonds of the methylcyclopentane (MCP) and ethylcyclopentane ring that are formed by C-atoms with a relatively low electron density. It might have been assumed that the pattern established in [1, 2] would also be correct in the case of analogous reactions of other hydrocarbons. To test this hypothesis, in the present work we investigated the influence of the pressure of H_2 on the direction of demethylation of 2-methylhexane (2MH) and studied the electronic structure of its molecule.

EXPERIMENTAL METHOD

The demethylation of 2MH may occur in two directions: cleavage of the $CH_2—CH_3$ bond leads to 2-methylpentane (2MP), while in the case of cleavage of the $CH—CH_3$ bond, n-hexane (NH) is formed. The change in the direction of demethylation of 2MH was evaluated according to the change in the ratio NH : 2MP. All the experiments were conducted over 20% Pt/C at 375°, total pressure 1 atm (atmospheric pressure) and 5 atm, and with various rates of delivery of 2MH, in order to establish whether the ratio NH : 2MP changes with changing degree of reaction. In all the experiments the partial pressure of 2MH remained constant (0.2 atm) and the total pressure was varied by varying p_{H_2} from 0.8 to 4.8 atm. Experiments at

TABLE 1. Conversions of 2-Methylhexane over 20% Platinized Charcoal (375°, partial pressure of 2-methylhexane 0.2 atm)

Rate of delivery of 2-methylhexane, mole/h per gram of catalyst $\cdot 10^{-3}$	Conversion of 2-methylhexane to reaction products, %			Content in catalyzates, %			Ratio n-hexane; 2-methylpentane
	hydrogenolysis	isomerization	dehydrocyclization	isopentane	2-methylpentane	n-hexane	
			Total pressure 1 atm				
25	1.2	13.6	5.6	0.17	0.53	0.46	0.87
77	0.5	8.2	1.8	0.11	0.22	0.19	0.87
78	0.7	10.8	1.6	0.13	0.28	0.23	0.82
						Average	0.85
			Total pressure 5 atm				
26	2.1	7.8	4.2	0.24	0.9	1.0	1.13
78	0.5	2.5	0.9	0.05	0.23	0.22	0.96
82	0.8	4.1	1.7	0.09	0.34	0.36	1.05
						Average	1.05

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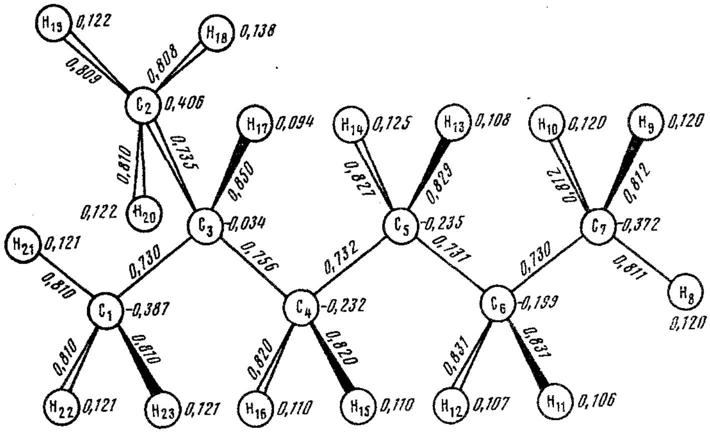

Fig. 1. Charges on the atoms and populations of the bonds according to Mulliken in the 2-methylhexane molecule.

1 and 5 atm were alternated. The method of analysis of the catalyzates differed from that described in [3] only by the use of n-octane as an internal standard. The basic results of the experiments are summarized in Table 1. Under the conditions selected, the yields of the products of demethylation did not exceed 2%, and, consequently, possible secondary reactions could not significantly change the ratio of these products. The reactions of isomerization and dehydrocyclization of 2MH reached a substantially greater depth (the products of the latter consisted chiefly of MCP and toluene).

RESULTS AND DISCUSSION

From the table data it follows that increasing p_{H_2} from 0.8 to 4.8 atm led to an increase in the ratio NH : 2MP from an average of 0.85 to 1.05. The presence of MCP in the catalyzates permitted us to assume the possibility of the formation of NH and 2MP by hydrogenolysis of the ring of MCP, and not demethylation of 2MH. Such an assumption was not confirmed: the ratio NH : 2MP in the experiments with MCP (conducted under the conditions described above) was approximately half that in the experiments with 2MH. Moreover, only traces of 2-methylpentane, which was formed in substantial amounts in the hydrogenolysis of MCP, were present in catalyzates of 2MH. Thus, the H_2 pressure promotes elimination of a CH_3 group bonded to the tertiary atom in the 2MH molecule. Then we investigated the electronic structure of 2MH in the conformation presented in Fig. 1. Here C_1, C_3, C_4, C_5, C_6, C_7, H_8, and H_{21} are situated in the plane of the figure. The atoms H_9 and H_{10}, H_{11} and H_{12}, H_{13} and H_{14}, H_{15} and H_{16}, H_{22} and H_{23} are arranged symmetrically to this plane. The atoms C_2, C_3, H_{17}, and H_{20} are in the plane β, perpendicular to the plane of the figure, while H_{18} and H_{19} are arranged symmetrically relative to the plane β. The calculation was performed according to [4], bringing in the parameters from [5]. The results of the calculation are cited in Fig. 1. A comparison of the experimental data permits us to conclude that the pattern established in [1, 2, 6, 7] is also correct for the demethylation of 2MH. Consequently, the interpretation of the influence of the pressure of H_2 on the direction of the hydrogenolysis of MCP and the dehydrocyclization of alkanes, proposed in [1, 6], can be extended to the demethylation of 2MH.

It can be assumed that demethylation catalysts possess the ability to adsorb hydrocarbon molecules primarily with the methyl groups, the C-atoms of which carry the maximum negative charges. Such catalysts, according to [1, 6] are characterized by a high electron donor capacity and ability to displace primarily hydride ions from hydrocarbon molecules during the formation of σ-complexes with them. However, when p_{H_2} is increased and H_2 is adsorbed on Pt, its electron acceptor capacity and ability to displace protons from hydrocarbon molecules increases [6]. The formation of σ-complexes according to a "proton" mechanism is characteristic of C-atoms with a minimum electron density, i.e., in the case of 2MH for a tertiary atom. Therefore, with increasing p_{H_2}, a fraction of 2MH molecules that enter into a reaction with the elimination of CH_3 from a tertiary atom with the formation of NH increases.

The conclusion of a high electron donor capacity of platinum deposited on charcoal was also drawn in [1], where it was shown that the hydrogenolysis of MCP over Pt-C occurs basically along the bonds of the ring formed by carbon atoms with maximum negative charges.

CONCLUSIONS

1. The hydrogen pressure changes the direction of the demethylation of 2-methylhexane over 20% Pt-C at 375°, promoting the elimination of methyl groups bonded to tertiary atoms.

2. The electronic structure of 2-methylhexane was studied, and it was shown that the carbon atoms of the methyl groups carry maximum negative charges, while the minimum electron density is concentrated on the tertiary atom.

LITERATURE CITED

1. A. M. Gyul'maliev, I. I. Levitskii, Kh. M. Minachev, and I. V. Stankevich, Izv. Akad. Nauk SSSR, Ser. Khim., 2475 (1972).
2. A. M. Boganov, A. M. Gyul'maliev, I. I. Levitskii, Kh. M. Minachev, and I. V. Stankevich, Izv. Akad. Nauk SSSR, Ser. Khim., 2257 (1973).
3. I. I. Levitskii, Kh. M. Minachev, and A. M. Boganov, Izv. Akad. Nauk SSSR, Ser. Khim., 762 (1973).
4. Yu. A. Kruglyak, D. D. Dyadyusha, V. A. Kuprevich, L. M. Podol'skaya, and G. I. Kagan, Methods of Calculation of Electron Density and Spectra of Molecules [in Russian], Naukova Dumka, Kiev (1969).
5. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).
6. I. I. Levitskii, Kh. M. Minachev, and E. A. Udal'tsova, Izv. Akad. Nauk SSSR, Ser. Khim., 300 (1973).
7. I. I. Levitskii, Kh. M. Minachev, and E. A. Udal'tsova, Izv. Akad. Nauk SSSR, Ser. Khim., 2031 (1973).