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Abstract

Full Text

Chemistry

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The reaction of dehydrogenation catalysis discovered by N. D. Zelinsky ([1]) has found broad application in the investigation of the chemical nature of cycloparaffin hydrocarbons contained in light petroleum fractions. However, up to the present time there have been no data in the literature on the use of this reaction for the purpose of elucidating the structure of saturated high-molecular-weight hydrocarbons of petroleum.

Fig. 1. Apparatus for dehydrogenation in the liquid phase. 1—metal bath for heating, 2—reaction vessel, 3—feed burette, 4—thermocouple pocket, 5—condenser, 6—burettes for measuring gas.

In carrying out systematic investigations of the chemical nature of high-molecular-weight petroleum hydrocarbons, we decided to test the applicability of the reaction of selective catalytic dehydrogenation for elucidating the structure of these hydrocarbons. For this purpose, synthetic hydrocarbons C_{20} —C_{32} were used, containing in the molecule 1-3 cyclohexane rings, 2 decalin rings, 1 cyclopentane ring, and 1 paraffin hydrocarbon of normal structure. The optimum conditions for catalytic dehydrogenation of high-molecular-weight cycloparaffin hydrocarbons in the liquid phase were first found, and the procedure for carrying out dehydrogenation was designed in apparatus form (Fig. 1).

Fig. 2

Figure 2: Fig. 2

Experimental Part

The catalyst—Pt on carbon, prepared according to B. A. Kazanskii (^{2}), in an amount of 15-18% relative to the substance subjected to dehydrogenation—is placed in flask 2 (Fig. 1), where it is reduced further in a stream of hydrogen with slow heating to 320° (2–3 hours). The catalyst is then kept for another 1 hour at 315°. After this, the hydrocarbon is fed in the liquid phase from burette (3) into the reaction flask, in which the reaction temperature (315°) is maintained constant. The supply of hydrogen to the system is stopped, and the entire system is isolated. The gas liberated as a result of the dehydrogenation reaction is cooled, passing through a condenser, to a temperature of 20° and is measured by two alternately operating burettes thermostated at 20°. As the burettes are filled, the gas is transferred to a gasometer.

In order to determine the behavior of hydrocarbons of different structure under conditions of selective catalytic dehydrogenation, the following individual compounds were synthesized: *n*-tetracosane, *n*-octadecylcyclopentane, 7-cyclohexyloctadecane, 1,5-dicyclohexyl-3-heptylpentane, 1,1-dicyclohexyldodecane, 1,5-dicyclohexyl-3-hexahydrobenzylpentane, 1,2-di-(1,3,5-trimethylcyclohexyl)ethane, and 2,11-didecahydronaphthyldodecane.

Compounds containing isolated cyclohexyl and decalin structures were obtained by hydrogenation of the corresponding phenyl and naphthyl derivatives of hydrocarbons, obtained by reactions of organomagnesium synthesis according to Grignard. The synthesis of these individual hydrocarbons will be reported separately.

Fig. 2. Change in the rate of hydrogen evolution (*a*) and in its total amount with time (*b*) during dehydrogenation of individual hydrocarbons.
1 —1,5-dicyclohexyl-3-hexahydrobenzylpentane;
2 —1,2-di-(1,3,5-trimethylcyclohexyl)ethane;
3 —7-cyclohexyloctadecane;
4 —2,11-didecahydronaphthyldodecane.

It was noted that dehydrogenation of individual hydrocarbon homologs of cyclohexane and decalin already proceeds at a temperature of 280°; however, the optimum temperature for dehydrogenation in the liquid phase in the presence of a platinum catalyst is 315–320°. At this temperature, dehydrogenation of all the hydrocarbons studied, containing both isolated and fused hexamethylene structures, is completed essentially within 5–6 hours, with practically complete absence of cracking phenomena.

Figure 2 shows the change in the rate of hydrogen evolution and in its total amount over time for individual hydrocarbons of different structure. The reaction temperature in all cases was 315°.

The liquid products of the dehydrogenation reaction were subjected to chromatographic separation on silica gel.

Table 1 gives the results of catalytic dehydrogenation of individual hydrocarbons and their mixtures.

The studies showed that the rates of hydrogen evolution during dehydrogenation of hydrocarbons of the most diverse structures become equal after 5–6 hours and become very small, i.e., the reaction is practically complete. An increase in the number of isolated hexamethylene rings in the hydrocarbon molecule and the presence of methyl groups in them have little effect on the dehydrogenation process.

A compound containing two condensed hexamethylene structures is dehydrogenated with greater difficulty.

In the dehydrogenation of 1,1-dicyclohexyldodecane, in addition to complete dehydrogenation, an experiment was carried out in which the dehydrogenation reaction was interrupted at the moment when the amount of hydrogen evolved was $\sim 1/2$ of the theoretical amount. Chromatographic separation of the reaction products from this experiment showed that they contained, in approximately equal amounts: (a) the initial 1,1-dicyclohexyldodecane, (b) the product of complete dehydrogenation of both cyclohexyl rings to benzene rings (1,1-diphenyldodecane), and (c) the product of half-dehydrogenation: 1-phenyl-1-cyclohexyldodecane. This result is experimental confirmation that dehydrogenation of cyclohexyl rings proceeds simultaneously in both directions, with formation of:

$$[\text{structure}] - \mathrm{C} - \mathrm{C}_{11} \qquad \text{and} \qquad [\text{structure}] - \mathrm{C} - \mathrm{C}_{11}$$

A paraffinic hydrocarbon of normal structure under the selected reaction conditions gives a yield of aromatic hydrocarbons of 1.8%, which indicates the insignificant role of dehydrocyclization of paraffinic chains.

In the study of *n*-octadecylcyclopentane under conditions of liquid-phase dehydrogenation, formation of aromatic hydrocarbons was observed in an amount of 6.1%. Condensation reactions are practically absent in all cases.

The study of the behavior of various structural groups of saturated high-molecular-weight hydrocarbons under conditions of liquid-phase dehydrogenation in the presence of Pt deposited on carbon and passivated Fe showed that the method of selective catalytic dehydrogenation in the liquid phase can be successfully applied to the investigation of fractions of saturated high-molecular-weight petroleum hydrocarbons whose molecules contain cycloparaffin rings, for the purpose of obtaining a more detailed characterization of their chemical nature.

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CITED LITERATURE

1. N. D. Zelinskii, ZhRFKhO, **43**, 1220 (1911).

2. B. A. Kazanskii, G. S. Landsberg, *Determination of the Individual Composition of Straight-Run Gasolines* (draft instructions), 1950.

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

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