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## Abstract

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# On the Mechanism of Isomerization and Deuteroexchange of Naphthenes in Liquid HBr

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In a previous work (1), the rate of the reaction of isotopic hydrogen exchange in cyclohexane with liquid DBr, catalyzed by $AlBr_3$, was measured. By measuring combination-scattering spectra it was established that, in this process, cyclohexane is isomerized into methylcyclopentane. In further development of this study, the results presented below were obtained from an investigation of the kinetics of the reactions of isomerization of methylcyclopentane and of hydrogen exchange in a series of naphthenic hydrocarbons dissolved in liquid hydrogen bromide enriched with deuterium (DBr).

The observations made lead to the conclusion that carbonium ions may participate in the course of the reactions named, which is important for interpreting their mechanism. Cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane of a high degree of purity were additionally subjected to chromatography on a column filled with silica gel and were dried with metallic sodium. They gave no formaldehyde reaction. $AlBr_3$ and $GaBr_3$, synthesized from the elements, were carefully purified, and weighed portions of them were taken without access of atmospheric moisture by means of a specially developed procedure (2). Experiments with solutions in liquid DBr were carried out by the procedure (3), with certain modifications. Measures were taken to reduce to a minimum impurities (unsaturated hydrocarbons, moisture, bromine, oxygen) that might affect the course of the isomerization reaction.

In determining the rate of isomerization of methylcyclopentane, the composition of the reaction mixture was established from measurements of the refractive index, using a calibration curve. On reaching equilibrium (25°), the isomerizate contained 12.5 mole % methylcyclopentane. The isomerization rate constant $k$ was calculated from the first-order equation (in $sec^{-1}$). It is proportional to the catalyst concentration $C$ (in moles per mole of liquid HBr): $k' = k/C = \text{const}$. In experiments with $AlBr_3$, $C$ was varied from $1.4 \cdot 10^{-3}$ to $6.9 \cdot 10^{-3}$, and the following values of $k \cdot 10^4 / C \cdot 10^3$ were obtained: 1.0; 1.4; 1.5; 1.3; 1.6; 1.8; 1.3; 0.8; 1.1; 1.1; 1.0; 1.2; mean 1.2. In experiments with $GaBr_3$, $C$ was varied from $1.7 \cdot 10^{-3}$ to $4.8 \cdot 10^{-3}$: $k \cdot 10^4 / C \cdot 10^3$: 0.2; 0.1; 0.2; 0.2; mean 0.2. Consequently, $AlBr_3$ proved to be approximately six times more active than $GaBr_3$. On addition of 0.03 g of cyclohexyl bromide to 0.3 g of methylcyclopentane, the rate of isomerization catalyzed by $AlBr_3$ increases: $k \cdot 10^4/C \cdot 10^3$: 10; 9; 9; mean 9.

Solutions of cyclopentane, methylcyclopentane, and cyclohexane in liquid HBr in the presence of $AlBr_3$, initially colorless, gradually turn yellow; the intensity of the color depends both on the concentration of $AlBr_3$ and on the duration of the experiment. In a solution of cyclohexane and methylcyclopentane at $C = (2\text{–}3) \cdot 10^{-2}$ mole $AlBr_3$ per mole HBr, a yellow-orange oil separates after 15–20 hr. A solution of cyclopentane begins to stratify after 6 hr at 25° when $C = 1.4 \cdot 10^{-2}$. All experiments on isomerization and deuteroexchange were carried out with homogeneous solutions. A solution of methylcyclohexane with an addition of $AlBr_3$ remained colorless and homogeneous even for several days. The refractive indices of cyclopentane

and methylcyclohexane did not change during the experiments within the accuracy limits of measurements with an Abbe-type refractometer. After the experiments with methylcyclopentane and cyclohexane, an isomerizate of equilibrium composition was obtained.

The rate of deuterium exchange was measured at 25°. The results were calculated in the same way as in (1). In the concentration interval $C = (0.2\text{—}1.3) \cdot 10^{-2}$ mole $AlBr_3$/mole HBr, the rate constants of deuterium exchange $k$ ($\text{sec}^{-1}$) are approximately proportional to $C$. We give the values of the relative rate constants $k' = k \cdot 10^5/C \cdot 10^2$*.

**Cyclopentane:** 5; 6; 5; 7; 4; 5; 6; 8; average 5.
**Methylcyclopentane:** 1.4; 1.4; 1.6; 0.6; 1.6; average 1.3.
**Cyclohexane:** 0.5; 0.4; 0.6; 0.6; 1.8; 1.6; 2.4; 0.7; 1.5; 1.2; 1.3; 0.6; 0.6; 1.9; 1.9; 2.1; 2.3; 2.8; 2.6; average 1.4.
**Methylcyclohexane:** 3; 3; 4; 4; 4; average 3.6.

The isotopic exchange of hydrogen in methylcyclopentane proceeds at a rate two orders of magnitude lower than the rate of isomerization. Consequently, regardless of whether the initial substance is methylcyclopentane or cyclohexane, the exchange reaction actually takes place in the equilibrium mixture of these hydrocarbons (equilibrium constant $k_{27^\circ} = 7.6$ (4)).

To clarify the mechanism of deuterium exchange, experiments were carried out in which cyclopentyl bromide or cyclopentene was added to cyclopentane in an amount of 0.1 mole per mole of hydrocarbon; cyclohexyl bromide or cyclohexene was added to cyclohexane and methylcyclohexane. The following values of $k_1' = k \cdot 10^5/C \cdot 10^2$ were obtained. Experiments with addition of bromide are marked with an asterisk.

**Cyclopentane:** 35; 52; 39; 25; 46; *50*; average 40.
**Cyclohexane:** 4; 4; 6; 4; 5; *7*; average 5.
**Methylcyclohexane:** 7; *10*; average 8.5.

Let us compare the values of the relative constants of the deuterium-exchange rate in experiments with and without additives:

| Hydrocarbon | $k_1'$ | $k'$ | $k_1' : k'$ |
|---|---|---|---|
| Cyclopentane | 40 | 5 | 8 |
| Methylcyclopentane | – | 1.3 | – |
| Cyclohexane | 5 | 1.4 | 3.5 |
| Methylcyclohexane | 9 | 3.6 | 2.6 |

It should be noted that the introduction into the reaction mixture of a halogen derivative or an unsaturated hydrocarbon not only increases the rate of deuterium exchange severalfold, but also enhances the intensity of the coloration of cyclopentane solutions and promotes the separation of oil in solutions of cyclohexane** and methylcyclohexane. This can be explained by an autocondensation reaction of the saturated hydrocarbon, which occurs in the presence of a halogen derivative under $AlBr_3$ catalysis and, according to Nenitzescu (5), proceeds through stages involving formation of a carbonium ion and abstraction of $H^-$ from the saturated hydrocarbon. The hydrogen in cyclohexyl bromide is exchanged rather rapidly for deuterium of liquid DBr upon addition of $AlBr_3$. This can be related to the observations of G. A. Razuvaev and co-workers (6), according to whom deuterium exchange occurs between deuterocyclohexane and cyclohexyl chloride at $t$. 18° under $AlCl_3$ catalysis.

## Discussion of the results obtained

A careful study of the isomerization of saturated hydrocarbons, in particular methylcyclopentane, has shown (7-9) that $AlBr_3$ (or $AlCl_3$) does not catalyze it in the absence of a promoter and that the reaction does not proceed even upon addition HBr (or HCl). The presence in the system of traces of an olefin is also necessary. Then an alkyl halide is obtained (it may also be added directly), and upon its subsequent reaction with $AlBr_3$, carbonium ions arise according to the equation

$$RBr + AlBr_3 \rightarrow R^+AlBr_4^-, \tag{I}$$

initiating the chain reaction of isomerization. However, as we have established, in the case when hydrogen bromide is not an additive but the solvent, $AlBr_3$ and $GaBr_3$ isomerize methylcyclopentane to cyclohexane (in the absence of an activator) under pure conditions, and the addition of cyclohexyl bromide merely

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* When portions of $AlBr_3$ were taken without using the procedure described in (2), approximately two times lower values of the rate constants were obtained.

** In one of the experiments the oil had the following constants: b.p. 213–215°; $n_D^{20}$ 1.5133. The properties and composition of the oil were not studied in more detail.

accelerates the reaction, whose rate at 25° is already considerable even without it.

Initiation of isomerization by formation of carbonium ions according to equation (I) is also possible if the catalyst is aluminum halide promoted with water. According to Nenitzescu ([5]), carbonium ions then arise owing to abstraction of hydrogen from a saturated hydrocarbon in the form of a hydride ion ($H^-$), which, not existing independently, immediately combines with a proton of the aluminum halide hydrate, which is a strong complex hydrohalic acid, with molecular hydrogen being formed; i.e., schematically the reaction is expressed by the equation*:

$$\equiv C - H + H^+ \rightarrow \equiv C^+ + H_2. \tag{II}$$

Indeed, Nenitzescu detected the formation of molecular hydrogen during the isomerization of methylcyclopentane. Solutions of $GaBr_3$ and $AlBr_3$ in liquid HBr are very strong acids (see ([10]), p. 63), and it is possible that the Nenitzescu mechanism is applicable to isomerization under these conditions. We have no direct experimental data concerning the formation of molecular hydrogen.

Let us now consider the results obtained with regard to deuterium exchange in naphthenic hydrocarbons. Beginning with Ingold, many authors (Barwell, Bick and Stevenson, D. N. Kursanov and V. N. Setkina, etc. ([10,11])) studied the isotopic exchange of hydrogen in saturated hydrocarbons with deuterosulfuric acid and established that hydrocarbons with a tertiary carbon atom participate in exchange reactions. A viewpoint was expressed and became generally accepted according to which sulfuric acid oxidizes the hydrogen atom of the methine group, and the carbonium ions arising in this process initiate the chain reaction of deuterium exchange.

In the deuterium exchange of naphthenes with a solution of $AlBr_3$ in liquid DBr discussed here, as in deuterium exchange with liquid DF ([12]), the oxidation stage is excluded, and therefore the mechanism proposed for hydrogen exchange with sulfuric acid proves inapplicable**. D. N. Kursanov noted that this limitation can be eliminated if, following Whitmore and Nenitzescu, it is accepted that carbonium ions are formed in hydrohalic-acid solutions according to equation (II).

The supposition that carbonium ions participate in carrying out the exchange reaction with a saturated hydrocarbon, catalyzed by $AlBr_3$ in liquid HBr, seems probable to us, since the addition to a naphthenic hydrocarbon of its halogen derivative considerably accelerates the exchange, and this is logical to connect with the formation of carbonium ions according to equation (I). Speaking

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* Other acid-base type reactions are also known in which molecular hydrogen and the hydride ion participate:

$$\equiv \mathrm{CH} + \mathrm{H}^- \rightarrow \equiv \mathrm{C}^- + \mathrm{H}_2 \qquad \text{(III)}$$

—a reaction between a hydrocarbon and a hydride with formation of a carbanion and hydrogen;

$$\equiv \mathrm{C}^- + \mathrm{H}_2 \rightarrow \equiv \mathrm{CH} + \mathrm{H}^- \qquad \text{(IV)}$$

—a reaction between a carbanion and molecular hydrogen, in which a hydrocarbon and hydride are formed (see ([10]), p. 113).

** Evidently, the condition of the presence of a tertiary carbon atom in the molecule of a saturated hydrocarbon is not mandatory either, since hydrogen exchange occurs in the cyclopentane molecule, and its constants do not change in the course of the exchange reaction.

more precisely, in a solvent with a low dielectric constant, such as liquid HBr ($DP_{25} = 4$), it is difficult to expect the formation of free ions; most likely, under the influence of $\mathrm{AlBr_3}$ the C—Br bond is polarized

$$\mathrm{R{-}Br} + \mathrm{AlBr_3} \rightarrow \overset{\delta+}{\mathrm{R}} - \overset{\delta-}{\mathrm{Br}} \cdot \mathrm{AlBr_3} \qquad \text{(V)}$$

and such a polarized complex participates in the transition state. In the absence of a halogen derivative of the hydrocarbon, “carbonium ions” may appear in a manner analogous to that assumed above in discussing the isomerization of methylcyclopentane in liquid HBr without a promoter. The detailed mechanisms of the processes of isomerization and deuterium exchange are different, as follows at least from the unequal rates of the reactions named.

The views set forth, whose hypothetical character must be emphasized, make it possible to encompass within a single approach three reactions taking place simultaneously in liquid DBr (isomerization, deuterium exchange, and condensation). In addition, the gap between the existing ideas about the mechanisms of the deuterium-exchange reaction in saturated hydrocarbons with sulfuric acid and with liquid hydrogen halides is eliminated.

Ingold believed that the only way in which sulfuric acid can participate in reactions of isotopic hydrogen exchange is by donating a proton (or deuteron). It is possible that the oxidizing action of sulfuric acid plays a certain role in exchange reactions, but apparently its high acidity is of primary importance. The existence of a linear dependence of the rate of the exchange reaction on the acidity function of sulfuric acid, and the absence of a dependence of the exchange rate on the degree of oxidation of the hydrocarbon, cannot be considered accidental ((10), p. 236). Characteristic of all reactions of isotopic hydrogen exchange in saturated hydrocarbons is that they can be carried out only with the aid of the strongest acids, because saturated hydrocarbons are among the weakest bases among hydrocarbons, as also follows from the concept of the acid–base nature of hydrogen exchange.

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