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ence of the presumably stronger acid "aluminum chloride"[1] no doubt results from the lack of mobility of the acid in this latter case.

The observation of tertiary-tertiary hydrogen exchange in isobutane in the presence of both sulfuric acid and the aluminum chloride catalyst, together with the correlation of the rate of this exchange reaction with acid strength in the case of sulfuric acid, makes possible a new quantitative measure of the strengths of very strong acids.

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Hydrogen Exchange Reactions of Paraffins in the Presence of Aluminum Chloride—Alumina Catalyst

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As a part of a comprehensive investigation of the reactions of hydrocarbons in the presence of acid-type catalysts by means of isotopic tracer methods,[1] we have recently studied the reactions of a group of monodeuteroparaffins in the presence of (1) a typical isomerization catalyst and (2) a typical alkylation catalyst. Inasmuch as certain features of the reactions are quite unexpected on the basis of hitherto published theories of the nature of acid catalyzed reactions, it seems desirable to present a summary of the results thus far obtained. This communication deals with the reactions of the seven monodeutero C_2, C_3, and C_4 paraffins in the presence of the isomerization catalyst. The accompanying communication deals with the reactions of the four monodeuterobutanes in the presence of the alkylation catalyst.

The isomerization catalyst consisted of alumina (4 mesh), vapor-impregnated with "anhydrous" aluminum chloride (0.25 g Al_2Cl_6 per g of catalyst and 0.7 mg-atom of hydrogen per mg-atom of chlorine). The catalyst (25 g) was contained in a vertical tube (50 cc) attached by standard taper joints to a vacuum system into which was incorporated a small volume, magnetic piston-type, circulating pump. In a typical experiment the reaction system was charged with 60 cc-atmos. of gas, the pump started, and one cc-atmos. samples were periodically removed for mass spectrometric analysis. The ratio of the amount of catalyst hydrogen to hydrocarbon deuterium was greater than 100.

During the time within which the experiments with the deuteroparaffins were carried out, the half-time for the equilibrium conversion of normal butane to isobutane increased from 180 minutes to 1900 minutes, owing to loss of isomerization activity of the catalyst. No disproportionation products were ever observed. No effort was made to reactivate the catalyst for isomerization (as by the addition of hydrogen chloride or water). Contrary to expectation, there was no detectable exchange of hydrogen between any of the paraffins (ethane-d_1, propane-1-d_1, propane-2-d_1, n-butane-1-d_1, n-butane-2-d_1, isobutane-1-d_1, and isobutane-2-d)[2] and the catalyst, as measured by the total deuterium content of the paraffins in the gas phase. However, as enumerated in the following paragraphs, a variety of intermolecular hydrogen exchange reactions was observed in the paraffins.

Extremely rapid intermolecular exchanges of secondary hydrogens in propane and of tertiary hydrogens in isobutane were found in the following reactions:

$$2CH_3CHDCH_3 \overset{\text{catalyst}}{\rightleftharpoons} CH_3CH_2CH_3+CH_3CD_2CH_3 \tag{1}$$

$$(CH_3)_3CD+(CH_3)_2(C^{13}H_3)CH \overset{\text{catalyst}}{\rightleftharpoons} (CH_3)_3CH+(CH_3)_2(C^{13}H_3)CD. \tag{2}$$

The half-time for equilibration at 25°C was 2.5 ±0.5 minutes for reaction (1) and less than two minutes for reaction (2). The temperature coefficient for the over-all reaction (1) was zero between 0° and 25°C, and the initial rate of this reaction was decreased by a factor of 5 by dilution with 90 percent argon.

A slow intermolecular exchange between primary and secondary hydrogens of propane was established by the formation of propane-1,2-d_2 and propane-d_0 from propane-1-d_1, as well as by the formation of propane-d_3 and propane-d_4 both from propane-1-d_1 and from propane-2-d_1.

Rapid intermolecular exchange of secondary hydrogens in n-butane was established by the reactions of n-butane-2-d_1. Slower intermolecular exchange of primary and secondary hydrogens in

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[1] J. Chem. Phys. **16**, 255 and 745 (1948).

[2] For clarity the substances properly designated 2-methylpropane-1-d and 2-methylpropane-2-d are designated herein as isobutane-1-d and isobutane-2-d, respectively.

TABLE I. Intermolecular hydrogen exchange reactions of ethane, propane, *n*-butane, and *i*-butane in the presence of aluminum chloride on alumina at 25°.

Reaction / Paraffin	Primary with primary	Primary with secondary	Primary with tertiary	Secondary with secondary	Tertiary with tertiary	Paraffin with catalyst
Ethane	no	—	—	—	—	no
Propane	?	very slow	—	fast	—	no
n-Butane	?	slow	—	fast	—	no
i-Butane	no	—	slow	—	very fast	no

normal butane (much more rapid than in propane) was demonstrated in the reactions of *n*-butane-1-d_1 and of *n*-butane-2-d_1. Both of these compounds produced the same final mixture of butanes after about five hours. The composition of this final mixture corresponded, within the experimental error, to a random distribution of hydrogen and deuterium among the butane molecules. The mole fraction of $C_4H_{10-n}D_n$ is given by $(10!/(10-n)!n!)\times(9/10)^{10-n}(1/10)^n$.

The intermolecular exchange reactions of *n*-butane-1-d_1 also had a zero temperature coefficient between 0° and 25°C, but the initial reaction rate was not changed by dilution with 90 percent argon. The rate of this reaction did not decrease during the period that the catalyst was used.

Isobutane was shown to undergo slow intermolecular exchange between primary and tertiary hydrogens through the formation from isobutane-2-*d* of isobutane-d_0 (33.3 percent), isobutane-d_2 (6.9 percent), isobutane-d_3 (4.9 percent), isobutane-d_4 (2.8 percent), isobutane-d_5 (1.9 percent), isobutane-d_6 (1.2 percent), isobutane-d_7 (0.5_8 percent), and isobutane-d_8 (0.2_7 percent) in 24 hours at 25°C. Isobutane-1-d_1 also showed intermolecular hydrogen exchange, but the product after 24 hours was quite different from that resulting from the reaction of isobutane-2-*d*. From isobutane-1-d_1 in 24 hours there was only formed 7 percent each of isobutane-d_0 and isobutane-d_2 and less than 0.2 percent isobutane-d_3. It will be noted that the concentrations of isobutane-d_6, isobutane-d_7, and isobutane-d_8 resulting from the reaction of isobutane-2-*d* are 100-, 1000-, and 10,000-fold greater, respectively, than their random distribution values.

The above described hydrogen exchange reactions of the various paraffins are summarized in Table I.

The fact that several of the isotopic species concentrations in the reaction of isobutane-2-*d* increase so far beyond their equilibrium values indicates that the life of the reactive complex which the molecule forms with the catalyst is sufficiently long that several exchanges of tertiary hydrogen from the gas phase with primary hydrogen of the adsorbed isobutane can take place before decomposition of the complex occurs.

The observation that only isobutane-d_0 and isobutane-d_2 were formed in significant amounts from isobutane-1-d_1 proves the extreme relative slowness of intermolecular exchange between primary hydrogens of isobutane.

Although the activity of the catalyst for isomerization of normal butane to isobutane decreased by a factor of ten during the course of this work, there was no corresponding change in the rate of the intermolecular exchange reactions as exemplified by the exchanges of *n*-butane-1-d_1. Thus it seems reasonable to conclude that different degrees of activation of the adsorbed paraffin are required for isomerization and for intermolecular exchange of hydrogens. Furthermore, the range of the rates of the various types of intermolecular hydrogen exchanges that a single paraffin can undergo clearly demonstrates different degrees of activation of the adsorbed paraffin for such exchanges.

These experiments provide no evidence that a primary transfer of hydrogen to the catalyst is a necessary prerequisite for the isomerization reaction since no hydrogen exchange with the catalyst was detectable under isomerization conditions. As will be shown in the accompanying communication, it seems that a necessary condition for hydrogen exchange with the catalyst is that another catalyst molecule can react with the reactive complex formed by the paraffin and the catalyst, a circumstance which can readily occur only in a liquid phase system. It will also be shown that hydrogen exchange with the catalyst can take place without isomerization.

In conclusion, there are in preparation papers which will describe in detail not only the results summarized in this and the accompanying note, but also the preparation, purity, and mass spectra of the various isotopic compounds employed in these investigations. For the purposes of these communications it will suffice to state that the upper limit to the olefin content of any one of the deuteroparaffins is 0.01 percent.