[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Catalytic Isomerization of Paraffin Hydrocarbons. III. The Course of the Reaction

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In formulating a mechanism for the aluminum halide catalyzed isomerization of paraffin hydrocarbons, one has at his disposal the following facts:

(1) Pure, dry aluminum bromide and chloride are completely inert toward paraffin hydrocarbons.[2,3,4] Solutions of aluminum bromide in *n*-butane are regular.[5]

(2) Addition of a hydrogen halide or substance capable of producing one by reaction with the aluminum halide (*e. g.*, water, *n*-butyl bromide) results in a catalytically active system.

Substances which, when added to aluminum bromide, produce groups of the type AlX_4^- are promoters for the catalytic isomerization. Also, boron fluoride is a promoter for aluminum bromide.

(3) Under mild conditions, isomerization is the only reaction observed with the lower paraffins. With the higher molecular weight paraffins, and with all paraffins at higher temperatures, simultaneous disproportionation and "cracking" may also occur.

The temperature coefficient of the isomerization is much lower than that of the cracking reaction.

(4) The primary reaction is always the interchange of a methyl group with a hydrogen atom two (sometimes three) carbon atoms removed.

(5) No *neo* paraffins have been prepared by pure isomerization reactions. Neopentane is resistant to isomerization and cracking by aluminum halides.

(6) As a last significant fact, it may be added that, under conditions where promoted aluminum halides will isomerize *n*-butane at an appreciable rate, none of the other common alkylation catalysts have any action on *n*-butane.

Although the results of all the experiments reported below are negative, they furnish an important clue to the mechanism of paraffin isomerization.

The following substances under the conditions noted were exposed in sealed Pyrex tubes with *n*-butane: Ten mole % BF_3 plus 25 mole % H_2O, at 85° for 23.5 hr.; 2 mole % BF_3 plus 1 mole % HCl, at 85° for 49 hr.; 6 mole % BF_3 plus 4 mole % HBr at room temp. for 291 hr.; 4 mole % BCl_3 plus 2 mole % HCl, 3 mole % BCl_3 plus 3 mole % HCl, and 3 mole % BCl_3 alone, all at 85° for 24 hr.; 5 mole % $FeCl_3$ plus 2 mole % HCl, 15 mole % $ZnCl_2$ plus 3 mole % HCl, 4 mole % $TiCl_4$ plus 2 mole % HCl, 6 mole % $SnCl_4$ plus 3 mole % HCl, all at 85° for 24 hr.; 60 mole % H_2SO_4 (96%), at room temp. for 32 days with occasional shaking; 70 mole % H_2SO_4 (100%), at room temp. for 214 days with occasional shaking; 40 mole % H_2SO_4 (20% fuming) at room temp. for 24 days with occasional shaking.

In none of these experiments did any reaction occur, with the exception of those with sulfuric acid, where gradual darkening of the acid layer was noted. No *i*-butane was detected in any run. In the case with 100% H_2SO_4, 96.5% of the *n*-butane charge was recovered and *ca.* 1% of low-boiling gases were evolved; the rest was presumably in the acid layer as oxidation products.

It is possible to outline a mechanism for the catalytic isomerization of paraffins which is in harmony with all the facts cited above and which leads to certain important predictions which may be experimentally tested.

The dimer bonds in Al_2Cl_6 or Al_2Br_6 must be broken before reaction can occur. It is not necessary that $HAlX_4$ be formed, for such substances as $NaAlBr_4$ and CH_3AlBr_4 are catalytically active. Therefore, the AlX_4^- group is provisionally considered as the catalyst.

Since isomerization under certain conditions may be completely without side reactions, the rearrangement is considered to occur in one more or less smooth act upon oriented collision of the paraffin with the catalyst, for simultaneous cracking and disproportionation would be expected if active fragments were relatively free to move in the system. Indeed, the high temperature coefficients of the side reactions indicate that the activated state of the catalyst–hydrocarbon complex can be torn into fragments by higher energy processes as well as being smoothly converted into isomers.

If the reaction is "intramolecular" (referring to the catalyst-paraffin activated complex and not to any over-all kinetic expression), then the catalyst must have at least two grips on a paraffin, one at a methyl group and one at a hydrogen. It is easiest to conceive of this as some type of cyclic reaction complex, with the usual space requirements.

One immediately thinks of two of the halogens of AlX_4^- acting as bases.[6] However, reaction

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[1] National Research Fellow in Chemistry, 1942–1943.

[2] Leighton and Heldman, THIS JOURNAL, 65, 2276 (1943).

[3] Heldman, *ibid.*, 66, 1786 (1944).

[4] The extensive data on the isomerization of paraffins through 1941 have been collected by Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1942. To avoid lengthy review of the literature, no references pertaining to the facts in this section will be made that can be found by consulting the above book or references 2 and 3.

[5] Heldman and Thurmond, THIS JOURNAL, 66, 427 (1944).

[6] The generalized acid-base concept of Lewis [*J. Franklin Inst.*, 226, 293 (1938)], which is used throughout this paper, provides the clearest basis and most concise terminology for catalytic reactions not involving oxidation–reduction or free radicals.

mechanisms based on this hypothesis are untenable because the simultaneous stripping of two acid groups from a paraffin molecule would mean that the latter was a dibasic acid far stronger than can reasonably be supposed, especially in view of the double negative charge left on the fragment. The conclusion must be drawn that the catalyst, AlX_4^-, acts as both an acid and a base.

The theory here presented is that aluminum exhibits a coördination number greater than four during isomerization catalysis[7]—*i. e.*, that the aluminum of AlX_4^- is still an acid. The detailed reaction mechanism may then be visualized as follows:

First there is an oriented collision of the catalyst with the paraffin to produce a configuration with a hydrogen from the third or fourth carbon in the paraffin chain near a halogen of the catalyst and the methyl group from the end of the chain near the aluminum. These configurations are chosen because of fact (4) given in the beginning of the paper and because these are the only configurations leading to sterically probable ring structures.

AlX_4^- acts as an acid toward the end methyl group and as a base toward the hydrogen, forming a transient activated complex with the methyl and hydrogen loosely attached to the catalyst and the hydrocarbon residue restrained from moving from the vicinity by the residual attraction of the $:CH_3$ and H or by the cage effect (if the isomerization is in the liquid phase).

There is then a shift of an electron pair from the middle to the new end carbon of the hydrocarbon fragment. Concomitantly, the fragment rotates with respect to the catalyst, so that it is brought into a new position with the $:CH_3$ and H adjacent to the middle and end carbon, respectively. Reattachment yields the 2- or 3-methyl isomer as the product.

At higher temperatures, where the rotation may become so violent as to remove the catalyst, with $:CH_3$ and/or H attached, from the hydrocarbon fragment, or with larger hydrocarbons, where the long tail may whip the reacting end out of the catalyst's reach during the transformation, the usual side reactions producing a variety of lower and higher boiling materials would occur, as observed.

If, perchance, the catalyst introduced is $HAlX_4$, it is possible that the H replaced on the hydrocarbon fragment would not be the same one removed, but rather the H from $HAlX_4$, since the two are practically equivalent, the one replaced depending on the direction of rotation.

In the previous paper,[3] the hypothesis was advanced that substances of the type $(Al_2Br_5)^+$-$(BF_3Br)^-$ were responsible for both the promoting effect of boron fluoride on aluminum bromide catalyzed paraffin isomerization and the observed production of boron bromide. If this is so, it is easy to understand the catalytic activity of $Al_2Br_5^+$ and like cationic substances on the basis of the reaction mechanism outlined above. $Al_2Br_5^+$ is undoubtedly a very strong acid (and, of course, a bromine base), and there are no prohibitive steric features.

On the other hand, Al_2Br_6 itself should not act as a catalyst for two reasons. First, the basicity of two of the bromines (those in the bridge between the aluminums) would be diminished, although this might not be sufficient to rule out catalytic activity. Second, and more important, is the fact that the rigidity of the two bridge bromines would prevent the distortion of the bromine–aluminum–bromine bond angles necessary to permit the aluminum to exhibit acid properties. With $Al_2Br_5^+$, no distortion would be necessary, since one aluminum already has an open orbital.

The lack of reactivity of neopentane is a pure steric effect. There is no objection to the formation of the catalyst–hydrocarbon intermediate, but the rotation necessary to yield an isomer is so hindered by the interference between the bromines and methyl forks as to be improbable. With a larger neoparaffin, cracking and disproportionation would be expected to be pronounced in comparison with other paraffins since these reactions are the only types possible. Indeed, $HAlBr_4$ exerts only a cracking action on neohexane even at low temperatures,[8] whereas the other hexanes under the same conditions undergo considerable isomerization and relatively small amounts of cracking.

It is corollary of the theory presented above that the catalyst be amphoteric, with a relatively critical balance between the acidity of the metal and basicity of the halogen. None of the other common Friedel–Crafts catalysts have activity in paraffin isomerization approaching that of the promoted aluminum halides.

The boron halides are not catalysts for paraffin isomerization simply because they are not amphoteric enough. Perhaps the clearest evidence on this point is that they do not dimerize, whereas aluminum chloride and bromide, which are weaker acids than the respective boron compounds, exhibit enough basicity of their halogens to form double molecules.

Sulfuric acid does not isomerize *n*-butane, as expected from the theory presented. The facts that the sulfuric acid catalyzed alkylation of butenes with *i*-butane gives products which cannot be explained on any simple basis,[9] and that the

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[7] Nozaki, THIS JOURNAL, **64**, 2920 (1942), suggested that aluminum attained a coördination number of five to account for kinetic results on the aluminum chloride catalyzed interchange of groups in aliphatic amines, and Lane, McCusker and Curran (*ibid.*, **64**, 2076 (1942)), have proposed a trigonal bipyramid structure for the aluminum chloride–dioxane complex to explain the low dipole moment of aluminum chloride in dioxane.

[8] Bishop, Dissertation, Western Reserve University, Cleveland, Ohio, 1942.

[9] See for example McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 647 (1941); Caesar and Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941).

action of the acid on isoparaffins is marked at room temperature,[10] are indicative of another type of mechanism for "isomerization" during alkylation. The same may be said for boron fluoride catalyzed alkylation. Grosse and Ipatieff's explanation for the large amounts of 2,3-dimethylbutane formed from ethylene and *i*-butane[11] is a thermodynamic impossibility.[12]

Boron fluoride has been reported as an isomerization catalyst.[13] However, Ipatieff and Grosse[14] obtained no isomerization of *i*-butane when it was subjected to boron fluoride, water, and nickel. While the validity of some of the patent claims may be doubtful, it would not be surprising if complexes formed by interaction of boron fluoride with the solid additives presumably present had catalytic properties.

At higher temperatures zinc chloride, ferric chloride, and stannic chloride are reported to be catalysts[15]; here the halides certainly have the desired acidic properties.

The mechanism presented leads to an important prediction, namely, that if the catalyst used is $RAlX_4$, *alkylation should be observed along with isomerization.* If the RX added splits out HX in the presence of Al_2X_6, then it is not possible to test the prediction by this method, for olefins will alkylate isoparaffins in the presence of promoted aluminum halides. However, certain aliphatic halides such as methyl bromide, methylene bromide, and ethyl bromide are apparently stable in the presence of aluminum bromide and can be used in critical experiments to test the prediction.

There is an indication that alkylation did occur in the experiment with methylene bromide in the preceding paper,[3] but the small amount of high-boiling material could not be identified. The expected pentane fraction in the methyl bromide experiment in the preceding paper would be so small as to be lost as column holdup in the fractionation analysis.

In the following paper are given the results of experiments with relatively large amounts of methyl and ethyl bromide, performed primarily as a test of the mechanism presented here.

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Summary

A mechanism for the aluminum halide catalyzed isomerization of paraffin hydrocarbons has been presented. The striking feature of the mechanism is that aluminum in AlX_4^- is still acidic. The mechanism accounts for the known facts of paraffin isomerization.

It is predicted as a consequence of the postulated mechanism that methyl bromide and ethyl bromide should alkylate paraffin hydrocarbons in the presence of aluminum bromide.

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[10] Whitmore and Johnson, THIS JOURNAL, 63, 1481 (1941).

[11] Grosse and Ipatieff, *J. Org. Chem.*, 8, 438 (1943).

[12] *Cf.* the equilibrium concentrations of the hexanes, Rossini, Prosen and Pitzer, *J. Res. Natl. Bur. Stds.*, 27, 529 (1941).

[13] Dutch Patent 48,596; U. S. Patents 2,257,896; 2,271,043.

[14] Ipatieff and Grosse, THIS JOURNAL, 57, 1616 (1935).

[15] See ref. 4, Appendix III.

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Aliphatic Friedel–Crafts Reactions. I. The Alkylation of Butanes by Methyl and Ethyl Bromide

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In the preceding paper,[2] a mechanism for the promoted aluminum halide catalyzed isomerization of paraffin hydrocarbons was presented.

The mechanism leads to the prediction that under certain conditions, when the promoter is methyl bromide or possibly ethyl bromide, and with a relatively light paraffin, such as a butane, alkylation should be observed along with isomerization of the paraffin. In short, a purely aliphatic Friedel–Crafts alkylation should occur.

The experiments here reported were conceived and carried out as a test of the proposed mechanism. Even small amounts of pentanes resulting from reaction in the systems *n*- or *i*-butane–methyl bromide–aluminum bromide would have been a positive test,[3] but actually it was found that substantial yields of *i*-pentane can be obtained in this manner as well as the isomer of the butane charge.

The pressure of other work has made it necessary to discontinue this line of work before a detailed study of the experimental conditions conducive to high yields of alkylate could be completed. However, the experiments presented unequivocally establish the occurrence of an aliphatic alkylation of the classical Friedel–Crafts type and are hence separately reported.

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[1] National Research Fellow in Chemistry, 1942–43.

[2] Heldman, THIS JOURNAL, 66, 1789 (1944).

[3] The amount of pentanes in the absence of methyl bromide is negligible at relatively low temperatures; see Leighton and Heldman, THIS JOURNAL, 65, 2276 (1943).