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The Exchange Reactions of Normal Paraffins and Unsubstituted Cycloparaffins with Alkyl Halides, Catalyzed by Aluminum Halides

BY CHARLES P. BREWER AND B. S. GREENSFELDER

In the presence of aluminum halide catalysts, hydrogen–halogen exchanges take place between primary, secondary or tertiary alkyl halides and hydrogen attached to the secondary carbon atoms of normal paraffins or unsubstituted cycloparaffins. These exchanges have been effected with cyclopentane, cyclohexane, propane and normal pentane to yield mainly secondary halides. It has also been shown that an olefin and hydrogen chloride can be substituted for a tertiary alkyl halide in the exchange reaction. The mechanism of the reaction involves the production of a carbonium ion from the normal paraffin or cycloparaffin by removal of a hydride ion from a secondary position in the molecule. These results extend the applicability of the carbonium ion concept of acid-catalyzed hydrocarbon reactions to important classes of compounds for which experimental evidence previously had not been supplied.

In a previous paper[1] a carbonium ion mechanism was applied to the acid-catalyzed reactions of hydrocarbons, in particular, those encountered in catalytic cracking. It was postulated for non-aromatics that a hydrocarbon must form a carbonium ion by interaction with a proton from the catalyst, or with another carbonium ion associated with the catalyst before it may crack. For olefins, the addition of a proton or carbonium ion to the double bond is sufficient. A different mechanism must be invoked for paraffins and cycloparaffins; for those containing tertiary carbon atoms, much experimental work has been reported in the literature, and has led to the reaction mechanism shown below. A similar mechanism has been proposed for normal paraffins but direct proof has been lacking. Our study now provides experimental evidence for the extension of these principles to normal paraffins and also to unsubstituted cycloparaffins.

The action of an aluminum halide on an alkyl halide produces a reaction intermediate which may be represented as an alkyl carbonium ion[2,3,4]; this intermediate may be characterized as a polarized alkyl halide–aluminum halide complex. Bartlett[5] and Schmerling[6] strongly support this viewpoint, and demonstrate that hydrogen–halogen exchange takes place between the complex and saturated hydrocarbons which contain a tertiary carbon atom. (Except in the case of bicyclo(2,2,1)-heptane[6] where unusual steric factors are present.) For such saturates, R'_3CH, the mechanism may be represented as

$$RX + AlX_3 \longrightarrow R^+AlX_4^-$$

$$R'_3CH + R^+AlX_4^- \longrightarrow R'_3C^+AlX_4^- + RH$$

$$R'_3C^+AlX_4^- \longrightarrow R'_3CX + AlX_3$$

This exchange reaction entails the production of a carbonium ion from a saturated tertiary hydrocarbon. Therefore, our study was directed to normal paraffins and unsubstituted cycloparaffins, which have been predicted previously to be less reactive in this respect.[6]

An important point to be verified[5] was the separation of hydrogen from hydrocarbon as a negative hydride ion, a step involving about 235 kcal. in the case of tertiary hydrogen, and even more for the less reactive secondary and primary hydrogen atoms.[7] For this purpose we have chosen a system wherein the fragment accepted by the hydrocarbon is halogen derived from an alkyl halide–aluminum halide complex, which can be considered to be negative.[2] Therefore, the hydrogen exchanged for halogen must be a hydride ion.

The results obtained by Nenitzescu and co-workers[8] in the reduction of certain alkyl halides by reaction with hydrocarbons in the presence of aluminum chloride can be explained by a mechanism similar to that above. Here again, saturates containing a tertiary carbon atom were used. Our experiments on saturates containing only primary and secondary carbon atoms are described below.

Experimental

Materials.—Aluminum chloride (Baker C.p.) was used as received. Aluminum bromide was obtained from A. D. McKay Company, New York. Alkyl halides (Eastman Kodak Company, White Label) were used as received. Cyclopentane (Phillips Petroleum Company) was redistilled to 49.0–49.2°. It contained 6.4% 2,2-dimethylbutane and had $n^{20}D$ 1.4028. Cyclohexane (du Pont) was above 99% purity by mass spectrometric analysis. Normal pentane (Phillips Petroleum Company) was above 98.5% purity. Propane was laboratory stock, at least 99% pure with less than 0.1% propylene. Isobutylene was laboratory stock and contained 1.2 mole per cent. butanes.

Procedure. (a) **Liquid Reactants.**—The apparatus consisted of a 1-liter, 2-necked, round-bottomed flask, connected by Tygon tubing from one opening to an ice-cooled condenser, manometer, water trap and Ascarite tube (to absorb hydrogen chloride and hydrogen bromide), carbon dioxide cold trap, and a gasholder, in this order. The apparatus was flushed with dry nitrogen, then the required amount of aluminum chloride (0.075 mole) was placed in the flask. Immediately the hydrocarbon (1.00 mole) and alkyl halide (0.50 mole), previously mixed, were added from a separatory funnel under slight pressure through the second flask opening, which was closed after the addition. Vigorous shaking by hand was carried out at once for the required time. To stop the reaction, a weighed large excess of water (usually 500 g.) at room temperature was added rapidly in the same manner as the reactants; no significant heating was observed. The flask was then cooled in ice. The top layer was separated, and to this were added any entrained hydrocarbon material in the water trap and the residue from the cold trap after expansion at room temperature into the gasholder. The combined product was then dried, weighed and distilled. The amounts of gas and of hydrogen chloride formed were obtained from the weights of the cold trap and water trap plus the Ascarite tube, respectively. When

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[1] Greensfelder, Voge and Good, *Ind. Eng. Chem.*, **41**, 2573 (1949).

[2] Fairbrother, *J. Chem. Soc.*, 503 (1937); 293 (1941); 503 (1945).

[3] Wertyporoch and Firla, *Z. physik. Chem.*, **162**, 398 (1932).

[4] Lebedev, *J. Phys. Chem.* (*U. S. S. R.*), **22**, 1509 (1948).

[5] Bartlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944).

[6] Schmerling and co-workers, *ibid.*, **67**, 1152 (1945); **68**, 153, 195 (1946).

[7] D. P. Stevenson, private communication.

[8] Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931); Nenitzescu and Dragan, *Ber.*, **66**, 1100, 1892 (1933); Nenitzescu and Isacescu, *ibid.*, **67B**, 1391 (1934).

aluminum bromide was used as a catalyst, a solution of the bromide in the hydrocarbon was placed in the flask, and the alkyl halide added.

(b) **Gaseous Reactants.**—The aluminum halide and alkyl halide were placed in a stainless steel bomb (325 ml. capacity), the aluminum halide being in a thin-walled glass ampoule. The bomb was closed, using a Teflon gasket, and the hydrocarbon added by expansion from a weighed vessel. The bomb was then shaken violently to break the ampoule and mix the reactants. After the desired reaction period, the liquid products were vented into water in the flask and collecting system described in (a) above, using the gaseous reactant pressure to force the products from the bomb. The remaining material in the bomb was then washed into the flask with a weighed quantity of water. In the case of the reaction with isobutylene and hydrogen chloride in place of an alkyl halide, the aluminum halide, saturated hydrocarbon and hydrogen chloride were placed in the bomb as described above, and then the liquid isobutylene forced in with nitrogen.

Identification of Products.—The gaseous products were identified with a mass spectrometer. After isolation by distillation, chloro- and bromocyclopentane, chlorocyclohexane and isopropyl bromide were identified by boiling point, refractive index, elementary analyses and comparison of the infrared absorption spectrum with that of the known pure chemical.

The bromides obtained from the exchange reaction with *n*-pentane were classified as primary, secondary or tertiary by applying the analysis of Michael and Leopold[9] in which secondary and tertiary bromides are determined by hydrolysis.

Liquid products other than those mentioned above were not closely examined. In general, a portion of the hydrocarbon feed and of the alkyl halide was recovered, together with unidentified products of the aluminum halide–alkyl halide reaction.

TABLE I

REACTIONS OF CYCLOPENTANE WITH ALKYL HALIDES AND ALUMINUM HALIDES

Charge: 1 mole cyclopentane, 0.5 mole alkyl halide, 0.075 mole aluminum halide; room temperature (22°)

Alkyl halide	Aluminum halide	Reaction time, min.	Cyclopentyl halide, % mole on cyclopentane
t-Butyl chloride	$AlCl_3$	1	3.7
t-Butyl chloride	$AlCl_3$	2	10.9
t-Butyl chloride	$AlCl_3$	5	10.5
t-Butyl chloride	$AlCl_3$	10	10.0
n-Propyl chloride	$AlCl_3$	2	3.1
Isopropyl chloride	$AlCl_3$	2	10.9
t-Butyl bromide	$AlBr_3$	2	23.6
t-Butyl bromide	$AlBr_3$	5	8.3[a]
t-Butyl bromide	$AlBr_3$	2	24.8[b]
Isobutylene–HCl[c]	$AlCl_3$	10	8.8

[a] Temperature, −45°. [b] Temperature, 0°. [c] 0.57 mole isobutylene, 0.44 mole hydrogen chloride.

TABLE II

EXCHANGE REACTIONS OF HYDROCARBONS WITH ALUMINUM HALIDES AND ALKYL HALIDES

Charge: 1 mole hydrocarbon, 0.5 mole alkyl halide, 0.075 mole aluminum halide, room temperature (22°)

Hydrocarbon	Alkyl halide	Aluminum halide	Time, min.	New halide	
				% mole on hydrocarbon charge	Identity
Cyclohexane	*t*-Butyl chloride	$AlCl_3$	2	3.3	Chlorocyclohexane
Cyclohexane	*t*-Butyl chloride	$AlCl_3$	5	8.3	Chlorocyclohexane
Cyclohexane	*t*-Butyl chloride	$AlCl_3$	8	5.2	Chlorocyclohexane
Propane	*t*-Butyl bromide	$AlBr_3$	5	7.9	Isopropyl bromide
n-Pentane	*t*-Butyl bromide	$AlBr_3$	2	3.1 4.4	*t*-Amyl bromide *s*-Bromopentanes[a]

[a] Traces of primary bromide were also found.

Results and Discussion

Our experiments demonstrate that this exchange reaction will take place directly between cyclopentane, cyclohexane, propane or normal pentane and *t*-butyl chloride, *t*-butyl bromide or *n*- or isopropyl chlorides under various experimental conditions in the presence of aluminum chloride or bromide. We also find that isobutylene and hydrogen chloride can be substituted for *t*-butyl chloride to yield an equivalent product. A summary of the results is given in Tables I and II.

Cyclopentane.—This compound is particularly useful in demonstrating the exchange reaction, since it does not isomerize or decompose under the experimental conditions. The production of cyclopentyl chloride by reaction of normal and isopropyl chlorides with cyclopentane, Table I, show that primary and secondary halides can be used for the exchange reaction as well as tertiary halides; however, *n*-propyl chloride may isomerize during reaction to the secondary halide. It is highly probable that substitution of the olefin + hydrogen halide for the corresponding alkyl halide can be made in any of the observed reactions, since aluminum halides are catalysts for the reaction $RCH{=}CH_2 + HX \rightleftarrows RCHXCH_3$. Table I shows isobutylene + hydrogen chloride to be equivalent to *t*-butyl chloride.

Both boron trifluoride and anhydrous ferric chloride proved ineffective in bringing about the exchange reaction with cyclopentane and *t*-butyl bromide and chloride, respectively. It appears that these weaker electrophilic catalysts cannot form a sufficiently reactive complex with the tertiary halide to enable successful attack upon the hydrocarbon.

Cyclohexane.—This compound is similar in type to cyclopentane, but isomerizes with aluminum halide catalysts to yield methylcyclopentane; $k_{eq.}$ is 0.123 at 25°.[10] It was, therefore, of considerable interest to find that the exchange product, Table II, consisted of chlorocyclohexane only, no 1-chloro-1-methylcyclopentane nor methylcyclopentane being found. In Bartlett's work, only 1-chloro-1-methylcyclohexane was isolated under similar reaction circumstances.[5] The cyclohexyl carbonium ion formed during the exchange apparently does not isomerize to the methylcyclopentyl form under our conditions before entering into stable combination with the chloride ion. In other words, the rates of formation and recombination of the cyclohexyl ion are greater than its rate of isomerization.

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(9) Michael and Leopold, *Ann.*, **379**, 263 (1911).

(10) Stevenson and Morgan, THIS JOURNAL, **70**, 2773 (1948).

Propane and Normal Pentane.—Since isopropyl bromide was produced from the exchange reaction of propane with *t*-butyl bromide and aluminum bromide, hydrogen–halogen exchange can take place directly at a secondary carbon atom in a normal paraffin. The additional evidence obtained with normal pentane is complicated by the occurrence of side reactions. The product from the reaction of this compound with aluminum bromide and *t*-butyl bromide consisted mainly of *t*-amyl bromide and *s*-amyl bromides in the ratio of 1 to 1.4, respectively. The tertiary bromide comes either from isopentane formed by isomerization, or from isomerized secondary bromides, but the large proportion of secondary bromides found indicates that considerable hydrogen–halogen exchange has taken place directly at secondary carbon atoms, since the reverse isomerization of the *t*-amyl bromide by aluminum bromide yields only 15 to 20% of the secondary isomer.[5] The direct reaction mechanism is also supported by the results previously obtained with cyclopentane, cyclohexane and propane. Attempts to effect an exchange with ethane and *t*-butyl bromide–aluminum bromide were unsuccessful.

These experiments show that direct hydrogen–halogen exchange takes place with normal paraffins or unsubstituted cycloparaffins by removal of a hydride ion from a secondary carbon atom. Therefore, these important types of hydrocarbons can react directly, and in the same manner as saturates containing a tertiary carbon atom, with an alkyl halide or an olefin and hydrogen halide. The results thus support the theory that the first step in the acid-catalyzed reactions of paraffins and cycloparaffins is the formation of a carbonium ion or "polarized complex" from these hydrocarbons. Validation of this type of reaction in terms of another system may be obtained from work in these laboratories[11] on the aluminum halide catalyzed hydrogen–deuterium exchange reactions of propane and the two butanes in which hydrogen and deuterium were transferred between secondary positions and between primary and secondary positions in both propane and *n*-butane, and between primary and tertiary positions in isobutane. The unreactivity of ethane also was demonstrated by this work. Furthermore, great differences in the relative rates of isomerization and hydrogen exchange were noted, corresponding to our findings on the lack of isomerization of cyclohexane.

No evidence has been obtained by us for the direct reaction of a proton with a paraffin or cycloparaffin to yield hydrogen and the corresponding carbonium ion. Much evidence has been presented, however, that acid-catalyzed reactions involving only paraffins, such as isomerization, are strongly accelerated by the presence of very small amounts of olefins[12] which provide initiatory carbonium ions by the addition of protons. Studies in these laboratories with butanes and sulfuric acid again indicate the important effect of small amounts of olefin both on the initiatory step and rate of hydrogen and deuterium exchange.[13] Thereafter the reaction may proceed chain-wise without further supply of olefinic promoter. In the catalytic cracking of saturates,[1] the small amounts of olefin required can be supplied readily by incipient thermal cracking of saturates at the high temperatures (400 to 550°) ordinarily employed in this process.

[11] Wagner, Beeck, Otvos and Stevenson, *J. Chem. Phys.*, **17**, 419 (1949).

[12] Pines and Wackher, THIS JOURNAL, **68**, 595 (1946).

[13] Beeck, Otvos, Stevenson and Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

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Determination of Dissociation Constants in a Mixture of Two Weak Acids by Electromotive Force Measurements

BY ROGER G. BATES

The simultaneous dissociation of two weak acids in a mixture is considered. An electromotive force method that permits the determination of the product of the two dissociation constants when one is known is described. This method can be applied advantageously in the study of moderately strong acids. To illustrate the procedure, the dissociation constant of acetic acid at 25° is evaluated from e.m.f. data for five mixtures of sodium acetate, formic acid and potassium chloride. The result is in agreement with accepted values.

The electromotive force, E, of the cell

Pt; H_2 (*g.*, 1 atm.), buffer solution, MCl, AgCl; Ag

furnishes the value of $-\log (f_H f_{Cl} m_H)$, for convenience termed *pw*H, in the buffered chloride solution by the equation

$$pw\mathrm{H} \equiv -\log (f_H f_{Cl} m_H) = (E - E^0)F/(2.3026\ RT) + \log m_{Cl} \quad (1)$$

where E^0 is the standard potential of the cell, m is molality and f is the molal activity coefficient. If the hydrogen ion concentration in the buffer solution is governed by the dissociation of a single weak electrolyte, equation (1) can be combined with the mass law expression for this dissociative equilibrium and the thermodynamic dissociation constant obtained by extrapolation of a function of the e.m.f. to zero ionic strength.[1]

When the hydrogen ion concentration in the buffer solution depends upon the dissociation of more than one acidic or basic group, *pw*H can also be expressed in terms of the dissociation constants for these equilibria. In an earlier contribution,[2] the determination of the product of the dissociation constants for two successive overlapping steps in

[1] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

[2] R. G. Bates, *ibid.*, **70**, 1579 (1948).