

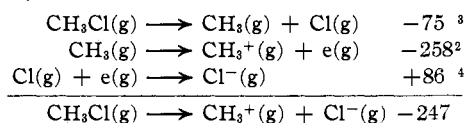
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Carbonium Ions and the Hydrolysis of Alkyl Halides

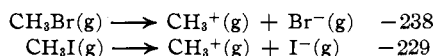
BY R. A. OGG, JR.

A considerable controversy has developed concerning interpretation of the rates of alkyl halide hydrolysis by neutral water (as distinguished from substitution reaction with hydroxyl ion).¹ Hughes and Ingold assume that the mechanism embodies a slow unimolecular dissociation of the alkyl halide into halide ion and organic cation with an incomplete valence shell (an "open sextet"), followed by the rapid reaction of this cation with water to yield alcohol and hydrogen ion. Olson and Halford, as well as Taylor, conclude that the rate determining step is a bimolecular reaction of a water molecule with alkyl halide to yield halide ion and a cation whose valence shell is completed by coordination of a previously unshared electron pair of a water molecule. The further complications suggested by Hammett do not affect the important distinction between these mechanisms. The author wishes to show that consideration of the energetics of the various reactions allows an unequivocal decision as to the mechanism of methyl halide hydrolysis.

The energy of dissociation of a gaseous methyl halide into gaseous ions has been made accessible to calculation by the determination of the ionization potential of methyl radical.² The application of Hess' law in the case of methyl chloride is given below. The energies of reaction are given in kilocalories per mole, roughed off to the nearest whole number (because of experimental uncertainties).



Similarly, one finds



The energies of dissociation³ of CH_3Br and CH_3I are taken, respectively, as 62 and 45 kcal., and the electron affinities⁴ of Br and I as 82 and 74 kcal. While the estimated energy effects apply to reac-

(1) For a recent list of important references, see W. Taylor, *THIS JOURNAL*, **60**, 2094 (1938).

(2) R. G. J. Fraser and T. N. Jewett, *Phys. Rev.*, **50**, 1091 (1936); *Proc. Roy. Soc. (London)*, **A160**, 563 (1937).

(3) N. V. Sidgwick, "The Covalent Bond in Chemistry," G. F. Baker Lectures, Cornell University, 1932.

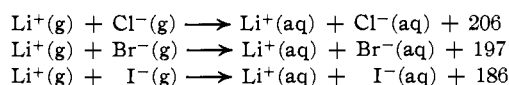
(4) J. E. Mayer and L. Helmholz, *Z. Physik*, **75**, 19 (1932).

tions at absolute zero, for purposes of this discussion they are not significantly different from the reaction energies at moderate temperatures (a few hundred degrees absolute).

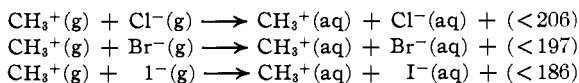
To estimate the energy effects for the corresponding processes in aqueous solution, it is necessary to know the energies of solution of the various substances in water. Energies of solution of gaseous methyl halides in water have not been determined. However, the energies of solution of the liquid halides are certainly small, and will be taken as zero. The energy of vaporization of the liquid halide then gives the desired quantity.

If the methyl ion in solution retains its open sextet of valence electrons, as assumed by Hughes and Ingold, then its solvation energy must arise from essentially the same factors contributing to the solvation energy of positive ions of noble gas type—*i. e.*, alkali metal ions. The hydration energy⁴ of alkali metal ions is an inverse function of the ionic "size"—*i. e.*, of the effective extension of electron charge density. Since the methyl ion has eight electrons and a nuclear charge distributed over four centers, its spatial extension of electron charge density is certainly greater than that of lithium ion (with only two electrons), and in fact is probably similar to that of sodium ion (ten electrons). Hence the hydration energy of lithium ion safely may be taken as an upper limit for the hydration energy of methyl ion with an open sextet of electrons.

The following hydration energies⁴ are used

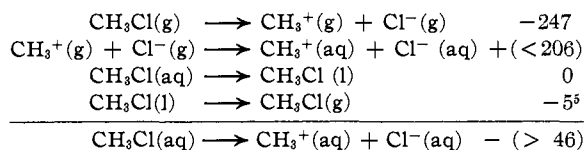


Therefore it is to be assumed

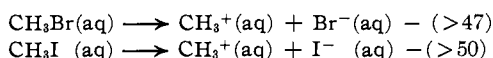


(As before, reaction energies are in kilocalories per mole.)

From the above, one may estimate a lower limit for the energy of dissociation of aqueous methyl chloride into aqueous chloride ion and aqueous methyl ion (with an open sextet).



Similarly



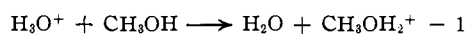
(The energies of vaporization⁵ of CH_3Br and CH_3I are taken, respectively, as 6 and 7 kcal.)

These figures must be regarded not only as lower limits for the dissociation energies, but as very much below the probable values. It was pointed out above that the "size" of a methyl ion with an open sextet is probably similar to that of a sodium ion. If the hydration energies⁴ of the two are assumed to be the same, then the corresponding dissociations of aqueous methyl chloride, bromide and iodide into ions are endothermic by 72, 72 and 74 kcal., respectively.

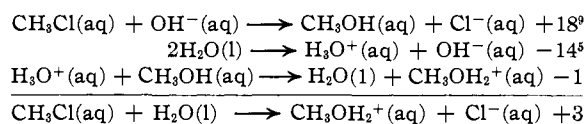
The unimolecular dissociations postulated by Hughes and Ingold would thus be endothermic by at least some 50 kcal. (and more probably by some seventy) in the case of methyl halides. The activation energies would in consequence be greater than 50 kcal. A unimolecular reaction with a normal temperature independent factor⁶ of some $10^{13} \text{ sec.}^{-1}$ and an activation energy of 50 kcal. would have a rate constant of only some $10^{-16} \text{ sec.}^{-1}$ at 100° . This must be regarded as an absolute upper limit for the rate constant of methyl halide hydrolysis at 100° by the Hughes-Ingold mechanism. Actually, the respective rate constants for the hydrolysis of methyl chloride, bromide and iodide in aqueous solution⁷ at 100° are 1.08×10^{-4} , 1.31×10^{-3} and $4.47 \times 10^{-4} \text{ sec.}^{-1}$. Thus the actual reactions are more rapid by many powers of ten than is possible by the Hughes-Ingold mechanism. The observed respective activation energies are some 22.7, 21.4 and 23.1 kcal. at 100° , and some 27.7, 26.5 and 28.1 kcal. at 25° —values far lower than the lowest possible limits for the Hughes-Ingold mechanism.

On the other hand, it can be shown that the energetics of the Olson-Halford mechanism are entirely compatible with the experimental data for methyl halide hydrolysis. It is to be noted that a methyl ion coordinated to a water molecule

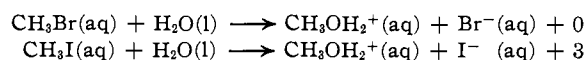
is identical with a proton coordinated to a methyl alcohol molecule—only one electronic structure being possible for CH_3OH_2^+ . Hence the basic strength of methyl alcohol gives a clue to the energy relations of CH_3OH_2^+ . For the distribution of protons between methyl alcohol and water molecules the equilibrium constant⁸ at 25° is some 0.235—water being the stronger base. It appears unlikely that the transfer of a proton from methyl alcohol to water will involve a large entropy change. If it is assumed that the free energy change is given entirely by the energy of reaction, this latter is equal to $RT \ln (1/0.235)$, which at 298° absolute is only about 1 kcal. Hence it is assumed



To estimate the energy of dissociation of aqueous methyl chloride into chloride ion and CH_3OH_2^+ the following summation is used.

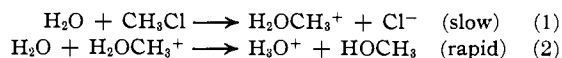


Similarly it is found



Thus dissociation of aqueous methyl halide into halide ion and CH_3OH_2^+ is a practically thermoneutral (or slightly exothermic) reaction. This is entirely compatible with the activation energy of the hydrolytic reaction by the Olson-Halford scheme. It is apparent that the reverse reaction (synthesis of methyl halide) must have a considerable activation energy. That is, the slowness of the reactions is due to a "true" activation energy.

It therefore appears that the experimental results of methyl halide hydrolysis are explicable in terms of the Olson-Halford mechanism, but not by that of Hughes and Ingold. The course of the reaction is to be pictured (using say CH_3Cl)



Reaction (1) is formally similar to a substitution reaction of alkyl halide with a negative ion¹⁰ in that one electron pair bond is broken and one is formed. Like the negative ion substitution reac-

(5) Landolt-Börnstein, "Tabellen."

(6) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," A. C. S. Monograph, Chemical Catalog Co., New York, N. Y., 1932.

(7) E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A164**, 295 (1938).

(8) H. Goldschmidt and P. Dahl, *Z. physik. Chem.*, **108**, 121 (1924).

(9) R. A. Ogg, Jr., *Trans. Faraday Soc.*, **31**, 1385 (1935).

(10) R. A. Ogg, Jr., and M. Polanyi, *ibid.*, **31**, 604 (1935).

tion, it is undoubtedly attended by Walden inversion.¹⁰

The dissociation energy of ethyl radical² into gaseous ethyl ion and electron is 245 kcal. per mole. If the bond energies are the same as for methyl halides, then the dissociation energies of gaseous ethyl halides into gaseous ethyl radical and halide ions are each some 13 kcal. less than the corresponding values for methyl halides. On the other hand, the "size" of the ethyl ion is undoubtedly greater than that of methyl ion, and in consequence its hydration energy (retaining the "open sextet" structure) must be less than that of methyl ion. Hence the calculated dissociation energies of aqueous ethyl halides into aqueous ethyl ion (with an "open sextet") and aqueous halide ions must be similar in magnitude to the corresponding values for methyl halides.

Only qualitative information is available concerning the rate of hydrolysis of ethyl halides by neutral water. At 100° the hydrolysis of ethyl iodide¹¹ is definitely slower than that of methyl iodide, but the two rates are of comparable magnitudes. A similar relation may be inferred for the hydrolysis of ethyl bromide and chloride. It thus seems probable that the activation energies for ethyl halide hydrolysis are similar to those for methyl halides, *i. e.*, some 25–30 kcal. From the preceding paragraph it is apparent that this is far less than the value demanded by the Hughes-Ingold mechanism. On the other hand, since the basic strengths of methyl and ethyl alcohols are similar, the dissociation of aqueous ethyl halide into $C_2H_5OH_2^+$ and halide ion is essentially thermoneutral. Thus the observed activation energy for ethyl halide hydrolysis is entirely compatible with the Olson-Halford mechanism.

For various other processes occurring in aqueous solution, in which CH_3^+ and $C_2H_5^+$ may be postulated as intermediates, energy calculations similar to the above indicate that the required activation energies are so large as to rule out the participation of these ions in reactions observable at ordinary temperatures. It is interesting to note the parallelism with the state of protons in aqueous solution. It is now generally recognized that the extremely large hydration energy of a proton is explicable only in terms of coordination with an unshared electron pair of a water molecule, forming H_3O^+ . Similarly, methyl and ethyl

"ions" in aqueous solution must be regarded as $CH_3OH_2^+$ and $C_2H_5OH_2^+$. Just as the concept of transient existence of "naked" protons has been discredited, so it appears that the concept of transient existence of CH_3^+ or $C_2H_5^+$ with an "open sextet" must be abandoned.

Considerations similar to the above apply to solvents other than water, whose molecules still possess one or more unshared electron pairs. Such solvents are ammonia, amines, sulfur dioxide, ethers, alcohols, carboxylic acids, etc. Since solvation energies of ions in such solvents do not differ radically from those in water, the production of methyl or ethyl ions with an open sextet demands activation energies comparable to those calculated for aqueous solutions, and hence is too slow to contribute to observable reactions. The real ionic intermediates are to be regarded as the coordination complexes of CH_3^+ or $C_2H_5^+$, such as $CH_3NH_3^+$, $CH_3OHCH_3^+$, etc.

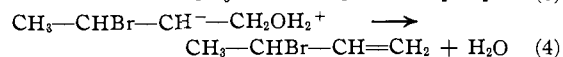
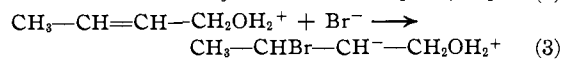
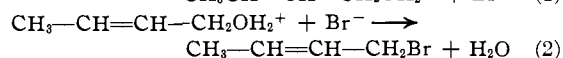
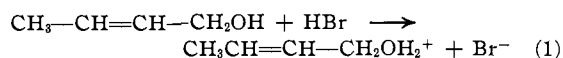
Extension of such numerical calculations to higher alkyl halides cannot be made reliably. Bond energies are more uncertain, and appropriate data regarding ionization potentials of higher alkyl radicals are completely lacking. However, it must be borne in mind that solvation energies of larger alkyl radicals (with an "open sextet") are necessarily considerably less than that of CH_3^+ . While it is probably true that the ionization potentials of large radicals are also less than that of methyl radical, it seems highly improbable that the difference of ionization potential and solvation energy can decrease sufficiently to make the Hughes-Ingold mechanism energetically feasible in any case. It appears that all "carbonium ions" are to be regarded as coordination complexes with a solvent molecule, and that any reaction calling for participation of ions with an "open sextet" will probably be too slow to be observable under ordinary conditions. The kinetic studies of the hydrolysis of higher alkyl halides are all to be interpreted in terms of the mechanism discussed above for methyl halides—*i. e.*, as a reaction with the solvent molecule, yielding halide ion and $R_3COH_2^+$.

Carbonium ions with an "open sextet" have been postulated freely in mechanisms for various molecular rearrangements. As a typical example, the formation of a mixture of crotyl bromide and methylvinylcarbinyl bromide from either of the pure carbinols and hydrogen bromide¹²

(11) J. Greenspan, S. Liotta and V. K. La Mer, *Trans. Faraday Soc.* **31**, 824 (1935).

(12) W. G. Young and J. F. Lane, *THIS JOURNAL*, **60**, 847 (1938).

has been interpreted in terms of resonance between the structures $\text{CH}_3\text{—CH}=\text{CH—CH}_2^+$ and $\text{CH}_3\text{—CH}^+\text{—CH}=\text{CH}_2$. If such ions are coordinated with solvent molecules, obviously the possibility of resonance disappears. The following alternative mechanism is entirely in accord with the considerations advanced above

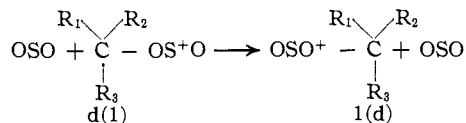


and similarly for methylvinylcarbinol. It should be noted that reaction (2) (of the usual type accompanied by Walden inversion) gives the normal product, while reactions (3) and (4) yield the rearranged product. Reactions (3) and (4) are similar to those previously postulated to explain the addition of halogens to ethylene linkages.¹³

The various cases in which rapid racemization of optically active carbonium ions has been noted¹⁴ are explicable in terms of an identical exchange reaction of the coordinated ion with the solvent molecules, as, say, in liquid sulfur dioxide.

(13) R. A. Ogg, Jr., *THIS JOURNAL*, **57**, 2727 (1935).

(14) E. S. Wallis and F. H. Adams, *ibid.*, **55**, 3838 (1933); E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378 (1933).



The above two examples are typical. It seems legitimate to state that it is never necessary to assume the existence of carbonium ions with an open sextet as intermediates in organic reactions, and that in view of the considerations of reaction energetics advanced above, preference is to be given to mechanisms not involving such ions.

Summary

It is shown that dissociation of a methyl halide (in aqueous solution) into a methyl ion with an "open sextet" and a halide ion is endothermic by at least some 50 kcal. per mole, and more probably by some 70 kcal. On the other hand, reaction with water to yield halide ion and the coordinated methyl ion CH_3OH_2^+ is practically thermoneutral. Comparison with the experimental data for methyl halide hydrolysis leads to rejection of the Hughes-Ingold mechanism (involving CH_3^+) in favor of the Olson-Halford mechanism (involving CH_3OH_2^+).

It is suggested that carbonium ions with an open sextet never play an appreciable role in observable organic reactions, and that mechanisms employing such ions must be abandoned.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA]

Physical Studies of Non-aqueous Solvates. III. The Vapor Pressure of Zinc Bromide-Diethyl Ether Solutions

BY H. H. ROWLEY AND FLORENCE V. OLSON¹

Considerable work has been reported on the preparation and properties of magnesium bromide-diethyl ether systems.²⁻⁴ Extension of the investigation of non-aqueous solvates would naturally include systems resembling the one already mentioned. The zinc bromide-diethyl ether system was chosen for this investigation since zinc belongs to the same periodic group as magnesium

(1) Present address: Women's College of the University of North Carolina, Greensboro, N. C.

(2) B. N. Menshutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

(3) J. Meisenheimer and J. Casper, *Ber.*, **54B**, 1655 (1921); J. Meisenheimer, E. Piper and H. Lange, *Z. anorg. allgem. Chem.*, **147**, 331 (1925).

(4) (a) W. V. Evans and H. H. Rowley, *THIS JOURNAL*, **52**, 3523 (1930); (b) H. H. Rowley, *ibid.*, **55**, 1337 (1936); (c) H. H. Rowley, *ibid.*, **59**, 621 (1937).

and the formulas of the compounds of the two metals are similar. Further, zinc, like magnesium, adds to alkyl halides in an ether medium to form organo-metallic compounds.

One of the first to report in the literature on zinc bromide diethyl etherates was Nickles,⁵ who found them to be quite unstable. Raynaud⁶ later prepared zinc bromide, using Nickles' method. The two layer system first formed, the lower layer of which was reddish in color, disappeared on further addition of bromine to give a homogeneous, brownish-violet liquid. Removal of excess ether left a

(5) M. J. Nickles, *Compt. rend.*, **52**, 396, 869 (1861).

(6) A. Raynaud, *Bull. soc. chim.*, **39**, 195 (1926).