On the Rate of Ionization in Aqueous Solution of the CarbonHydrogen Bond in Aliphatic Compounds

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The rate at which the carbon-hydrogen bond ionizes to give protons is studied by exchange with deuterium oxide. A base catalyst such as OD^- ion is used. A large number of data are correlated in terms of the rate constants k at 25°. In some cases the calculations required to bring the data to comparable conditions are only approximate. The data are restricted to aliphatic compounds and include measurements on nitrohydrocarbons, acetone, acetaldehyde, acetic acid, acetonitrile, methyl sulfonic acid, halogenated compounds and hydroxl compounds. The velocity constants of ionization range from 10^3 to 10^{-7}, and the order in which the various substituents affect the rate of the CH ionization is given. The influence of substitution on the ionization constants of carboxylic acids has long been studied from the standpoint of thermodynamics. The ionization of CH is a simpler process than the ionization of COOH and it should be possible to learn more of the mechanism through kinetics.

A T THE meeting of the Faraday Society in September 1937 C. L. Wilson[1] gave a report on the ionization rate of carbon-hydrogen bonds and some weeks later at the symposium on deuterium of the Bunsengesellschaft, Ingold and Wilson[2] summarized our knowledge of exchange reactions of light and heavy hydrogen. It is proposed to deal only with a small section of the problems discussed in these reports. We will restrict ourselves to the ionization of the C−H bond in the most simple aliphatic compounds and discuss only exchange reactions in D_2O catalyzed by bases; for base catalyzed reactions alone bear a direct simple relation to the velocity of ionization. During the last few years we have been interested in the deuterium exchange of these compounds and we will try in the following paper to compare the influence of different substituents in methane on the ease of this ionization. For a comparison we must, for the most part, use our own measurements on the velocity of deuterium uptake. But in some important cases we will supplement and compare our results with those obtained by other authors or by other methods.

It is well known that other methods exist for measuring this ionization rate. The direct method of electrical conductivity measurement is available only in the special case of nitrocompounds

and, this, indeed, is very fortunate, since the ordinary exchange methods cannot be applied here. Moreover there are many reactions, such as halogenations, tautomerizations, racemizations, aldol condensations and other similar processes, the velocity of which is determined by the carbon hydrogen ionization. It is often possible to draw conclusions concerning the ionization rate from the velocity of these reactions.

It is generally agreed that the base (in the Brønsted sense) catalyzes the exchange of light hydrogen and deuterium by removing a proton from the compound, and that the solvent D_2O (or another deuteron-donator) returns a deuteron at the position where the proton was removed. In the case of all compounds which will be considered here with the exception of the nitroparaffins in alkaline solution, the hydrogen is much more slowly removed from the compound than it is returned. This is shown by the very low degree of ionization of these compounds at equilibrium. Therefore the rate of ionization is equal to the rate of formation of the monosubstituted compound. We will call this velocity the "deuterium exchange rate" even in the case, where the compound contains several equivalent hydrogen atoms as for example acetone. The deuterium exchange rate depends on the nature of the catalyzing base. In most of our experiments the base used was the OD^- ion, so we will, if possible, relate all our velocities to this base and give the ionization rate constants with

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633.
[1] C. L. Wilson, Trans. Faraday Soc. **34**, 175 (1938).
[2] C. K. Ingold and C. L. Wilson, Zeits. f. Electrochem. **44**, 62 (1938).

respect to $1n$ OD⁻ concentration and 25°C (calculated with natural logarithms). In cases where no measurements with this base at 25°C were available, we tried to obtain approximate values by calculations from results obtained at other experimental conditions. If the experiments were carried out with OH⁻ ions and not with OD⁻ ions, we raised the value by about 40 percent, an amount which Wynne-Jones[3] and La Mer[4] have found in some special cases. In the case of measurements at higher temperatures, such as with acetic acid, log k was extrapolated linearly against $1/T$ to 25°C. Exchange reactions carried out at lower OD⁻ concentrations were calculated assuming their velocities to be proportional to the OD⁻ concentration. Consequently the accuracy of the figures given in the following sections varies greatly and is sometimes difficult to estimate. In several cases, also velocity constants for CH_3COO^- or water molecules as catalyst are given.

1. NITROMETHANE

We place nitromethane at the head of our discussion on account of its especially high tendency to C–H ionization. Pedersen[5] showed that in alkaline solutions the velocity of neutralization which can be followed at 0° by electrical conductivity measurement, is equal to the rate of this ionization. Maron and La Mer[4] measured the velocity in light water and found $k = 237$ min.⁻¹ for $1n$ OH⁻ concentration at 0°C. We can obtain an approximate value for $1n$ OD⁻ concentration at the same temperature by raising this value by approximately 40 percent, a factor found to hold for *nitroethane*, and assuming the same activation heat of 11.5 kcal. We find at 25°C, $k = 2 \cdot 10^3$ min.⁻¹.

This value agrees to some extent with results obtained by Junell.[6] He did not determine the concentration of ions by conductivity measurements but by the quantity of bromine used, when an excess of strongly acid bromine solution was added to the alkaline medium, in which the ionization proceeded. Since however this method

is not free from objections, it is possible to account for the observed differences.

These objections do not hold for a measurement of the ionization velocity with the acetate ion as catalyst, because in this case the bromination can be followed in a buffer solution of acetic acid and an acetate. It is to be expected, that in this case the rate of bromination will correspond exactly with the rate of ionization (see acetone). The velocity constant, k, at 25°C and $1n$ acetate concentration was found to be $4.0 \cdot 10^{-3}$ min.⁻¹ in D_2O and $4.5 \cdot 10^{-3}$ min.⁻¹ in H_2O.[7, *]

The strong tendency of the nitroparaffins to C–H ionization can be explained from a quantum-mechanical viewpoint as a resonance effect between the two (mesomeric) forms of the ion: $^-CH_2NO_2 \leftrightarrow CH_2 = NO_2^-$. In this manner the heat of ionization is lowered.

2. ACETONE

In a dilute solution of acetone in deuterium oxide containing KOD, the exchange of light and heavy hydrogen proceeds quite rapidly. Since for a measurement of the reaction rate a separation of acetone and water is necessary and since this separation requires time, only very dilute alkali solutions (< 0.01 normal) can be used. The separation of acetone and water was effected by distillation and the amount of deuterium taken up by the acetone was determined by drying and burning it. The velocity was found to be proportional to the OD⁻ concentration and the velocity constant of the exchange, i.e., of the ionization at $1n$ OD⁻ concentration was 14.5 min.⁻¹ at 25°C.[8]

It is interesting to compare this value with the velocity constant of the base catalyzed halogenation of acetone. Lapworth[9] has shown that the halogenation of acetone catalyzed by acids or bases, is independent of the concentration of halogen, from which it follows that the rate determining step of halogenation is a transformation of the ketone into a reactive form. There are good reasons to believe that in the case of base catalysis this reactive form is the ion

[3] K. F. Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).
[4] S. H. Maron and V. K. La Mer, J. Am. Chem. Soc. **60**, 2588 (1938).
[5] K. I. Pedersen, Dissert. Kopenhagen (1932).
[6] R. Junell, Dissert. Uppsala (1935).

[7] O. Reitz, Zeits. f. physik. Chemie **A176**, 363 (1936).
* The figure given by Reitz is calculated with decadic logarithms.
[8] W. D. Walters and K. F. Bonhoeffer, Zeits. f. physik. Chemie **A182**, 265 (1938).
[9] A. Lapworth, J. Chem. Soc. London **85**, 30 (1904).

$[CH_3COCH_2]^-$ resulting from the ionization of the CH bond. Now the quantitative measurement of the rate of halogenation is not as simple in the case of base catalysis as in the case of acid catalysis on account of side reactions which may take place in alkaline solutions and on account of the reaction of the halogen with the alkali itself. Nevertheless, Dawson and Key[10] succeeded in calculating from their measurements the rate constant of the iodination of acetone for 1 normal OH^- concentration at 25°C and found it to be 25 min.$^{-1}$.

This value although of the same order of magnitude as the value given by the exchange experiments, is almost twice as high. The difference becomes more noticeable when we consider that the iodination experiments were carried out with OH^- ions as catalyst and the exchange experiments with OD^- ions. We will therefore raise the iodination constant by 40 percent in order to get a value that is really comparable. In this manner we obtain a velocity constant of approximately 35 min.$^{-1}$ for the iodination catalyzed by OD^- ions. It is possible that the difference between the rates of iodination and exchange can be explained in the following way. Equality of both reaction constants is only to be expected if the product of iodination is the monosubstituted product. Indeed in the case of acid catalysis CH_2ICOCH_3 is formed, but there are reasons to doubt this for base catalysis. As we will show later it is very probable that in this case higher substituted products such as CI_3COCH_3 are formed. Therefore, it is very reasonable to suppose that the velocity constant for the iodination (as measured by the change in iodine concentration) can be about three times as high as the velocity constant of ionization.

The easy ionization of the C−H bond of acetone can be explained in a manner similar to that of the nitroparaffins. The ion formed by this ionization process is a resonance system which is represented by the two formulae

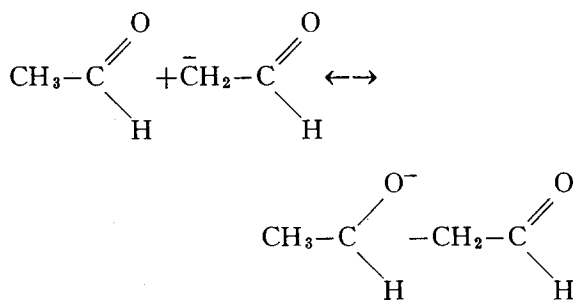$$^-CH_2-COCH_3 \leftrightarrow CH_2=CO^--CH_3.$$
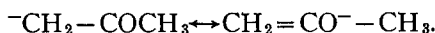
3. ACETALDEHYDE

In a dilute solution of acetaldehyde in deuterium oxide containing KOD there is a

rapid condensation reaction in which aldol is formed. This reaction proceeds more quickly than in the case of acetone where condensation also takes place. The primary aldol formed was isolated by ether extraction and did not contain any deuterium in the carbon-hydrogen linkage, as opposed to the diacetone alcohol which is the condensation product of acetone.[11] From this we can define an upper limit for the velocity of ionization of acetaldehyde. On the other hand, we have to consider that the mechanism of aldol condensation has a very definite formal resemblance to the mechanism of enolization which is expressed by the formulae

$$\cdots C - C \cdots \rightarrow \cdots C = C \cdots \quad \text{Enolization}$$
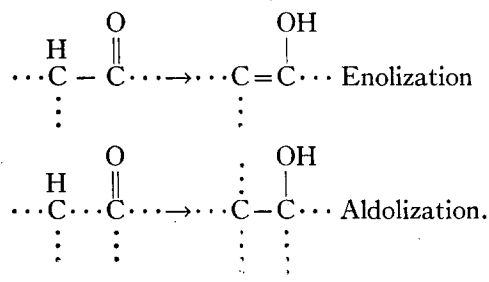
$$\cdots C \cdots C \cdots \rightarrow \cdots C - C \cdots \quad \text{Aldolization.}$$

This makes it more than probable that also in the base catalyzed aldolization the primary step is given by the ionization and that the reaction then proceeds as follows:

$$CH_3-C\underset{H}{\overset{O}{\diagup}} + ^-CH_2-C\underset{H}{\overset{O}{\diagup}} \leftrightarrow$$

$$CH_3-C\underset{H}{\overset{O^-}{\diagup}} -CH_2-C\underset{H}{\overset{O}{\diagup}}$$

Assuming this mechanism the velocity of aldolization must also be a lower limit of the velocity of ionization. We have therefore to conclude that the velocity of aldolization is identical with the velocity of ionization and that every acetaldehyde ion formed immediately gives aldol.[11] This assumption agrees with the statement of Bell[12] that the rate of aldolization is of the first order with respect to the acetaldehyde

[10] H. M. Dawson and A. Key, J. Chem. Soc. London 543, 2154 (1928).

[11] K. F. Bonhoeffer and W. D. Walters, Zeits. f. physik. Chemie A181, 447 (1938).

[12] R. P. Bell, J. Chem. Soc. London 1637 (1937).

since the rate determining process is the ionization. The velocity constant given by Bell* for $1n$ OH^- concentration (linearly extrapolated) is 8.0 min.$^{-1}$ at 25°. For comparison we must raise that value by about 40 percent, and we obtain the constant 11 min.$^{-1}$ for $1n$ OD^- concentration.

Acetaldehyde and acetone show therefore no appreciable difference in their ionization velocity.

4. Acetic Acid

In a dilute solution of an acetate in deuterium oxide containing an excess of KOD there is, at room temperature, no exchange of hydrogen and deuterium at the carbon atom. Exchange begins only at higher temperatures and requires many hours at 100°C. The process takes place between acetate ions and deuteroxylions. The rate of reaction was measured between 77°C and 206°C by determining the deuterium content of the salt.[13] This was obtained in a mixture with KCl after neutralization of the alkali and removal of the solvent.

At 100°C the velocity constant† was $1.8 \cdot 10^{-3}$ min.$^{-1}$ for $1n$ OD^- concentration. The constant at 25°C was extrapolated with the empirical equation

$$\log_{10} k_{\text{CH}_3\text{COO}^-, \text{ OD}^-} = 10.2 - \frac{22,000}{4.57T} \text{ min}^{-1}.,$$

from whence

$$k = 1 \cdot 10^{-6} \text{ min.}^{-1} \text{ at } 25°C.$$

This is a measurement of the influence of the COO^- group, but not of the $COOD$ group. The efficiency of the carboxyl group itself cannot be measured with any certainty. Considering the fact that the second dissociation constant of bivalent acids is much lower than the first constant, if both carboxyl groups are near to each other, it is to be expected that the CH_3 group of the acid molecule will ionize more readily than that of the electrically charged acetate ion. It is possible that the uptake of deuterium shown by a

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* k is calculated by Bell with decadic logarithms.
[13] L. D. C. Bok and K. H. Geib, Zeits. f. physik. Chemie **A183**, 353 (1939).
† The figures given by Bok and Geib have to be multiplied by three, since they give the exchange rate for a particular hydrogen atom of the methyl group and not for any one of the hydrogen atoms. Only the latter corresponds with our definition of exchange rate.

neutral acetate (without alkali addition) is caused by the reaction $CH_3COOH + OD^- \longleftrightarrow {}^-CH_2COOH + HOD$. This deuterium uptake was measured and from these measurements[13] the constant extrapolated to room temperature would be about 10^4 times higher than the value for the CH_3COO^- ion given above. This ratio would be higher than the ratio of the first and second dissociation constants of oxalic acid. In view of the uncertainty relating to the interpretation of the experimental results this question must remain open.

On the other hand, it is possible to give a value for *acetamide*.[14] Acetamide dissolved in alkaline deuterium oxide shows hydrolysis and deuterium exchange at the same time. The velocity constant for $1n$ OD^- concentration at 25°C is approximately $1 \cdot 10^{-3}$ min.$^{-1}$ i.e., more than 1000 times higher than that of the acetate ion.

The ionization rate constants of the esters of acetic acid are not yet known, because hydrolysis proceeds much faster than exchange in alkaline deuterium oxide. It is possible to say only that the exchange velocity constant of the methylester of acetic acid is less than 1 min.$^{-1}$. This, however, is not of great significance, since the constant is perhaps very much lower and of the order of the velocity constants of acetic acid and acetamide.

One can assume that the same resonance effects which are responsible for the ionization in the case of carbonyl compounds hold with respect to carboxyl and its derivatives but the reason why the carboxyl is less effective does not seem to be quite clear. On the other hand, it is remarkable that the exchange rate of the acetate ion is not very much higher than that of the methylsulfonate ion and that in the latter case a mesomeric effect should not exist.

5. Acetonitrile

In a dilute solution of acetonitrile in deuterium oxide containing KOD the exchange of hydrogen and deuterium in the methyl group proceeds 30 to 40 times faster than hydrolysis. The acetate formed by alkaline hydrolysis in D_2O contained much deuterium. This could not have been introduced by the exchange of the acetate itself on account of its low ionization rate. Assuming an

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[14] O. Reitz, Zeits. f. physik. Chemie **A183**, 371 (1939).

activation heat of about 20 kcal, the velocity constant of acetonitrile calculated from these experiments carried out at 35°C for $1n$ OD$^-$ concentration at 25°C is 2–$3 \cdot 10^{-3}$ min.$^{-1}$.[14] It is of the same order of magnitude as that of acetamide. The facility of ionization can be explained in the same way as with the former substances by considering the resonance effect of the ion $^-CH_2 - CN \leftrightarrow CH_2 = CN^-$.

6. Methyl Sulfonic Acid

In a dilute solution of sodium methylsulfonate in D$_2$O containing an excess of NaOD the exchange between hydrogen and deuterium at the carbon atom is slower than the exchange with potassium acetate under corresponding experimental conditions. In experiments at 100°C Hochberg found the rate constant of ionization to be about $1 \cdot 10^{-3}$ min.$^{-1}$ for $1n$ OD$^-$ concentration.[15]

In order to get an approximate value for 25°C we will assume that the heats of activation for the ionization of the acetate and the methylsulfonate ion are equal. On this assumption the ionization rate of the methylsulfonate ion is about $5 \cdot 10^{-7}$ min.$^{-1}$ at 25°C and $1n$ OD$^-$ concentration.

There is some difficulty here in assuming that resonance phenomena contribute to ionization. The SO linkage in compounds of this type is not a double bond but rather a semi-polar one, $S^+ - O^-$ and seems not to permit the existence of mesomeric forms.[16] Nevertheless the tendency to ionization in methylsulfonic acid is not very much less than in acetic acid and makes the existence of mesomeric forms not improbable.

7. Halogenated Compounds

The effect of halogen, hydroxyl or alkyl substitution has been measured only in those compounds which themselves show an appreciable tendency toward CH ionization.* Our knowledge of the influence of halogens is based on experiments with brominated nitroparaffins and acetones.

Junell[6] measured the bromination velocity in a $1n$ acid solution of bromosubstituted nitromethane and nitroethane catalyzed by the H$_2$O molecule as base. At 35°C he found the following values ($c_{H_2O} = 55.5$)

Nitromethane   Monobromonitromethane
$k = 9 \cdot 10^{-6}$ min.$^{-1}$, $k = 2.4 \cdot 10^{-3}$ min.$^{-1}$,

Dibromonitromethane
$1.2 \cdot 10^{-1}$ min.$^{-1}$.

Since the temperature coefficient has been measured for nitromethane and dibromonitromethane, we can calculate the corresponding values for 25°C and find

Nitromethane   Monobromonitromethane
$k = 3 \cdot 10^{-6}$ min.$^{-1}$, $8 \cdot 10^{-4}$ min.$^{-1}$,

Dibromonitromethane
$4 \cdot 10^{-2}$ min.$^{-1}$.

The rate constants with OD$^-$ as base catalyst have not been determined. Therefore we cannot give, for the influence of the halogens, values which are directly comparable with the other substituents. However, in any case it follows from the observations with H$_2$O as catalyst that the tendency to CH ionization is increased if an halogen is attached to the C atom.

Experiments of Watson and Yates[17] with *bromoacetones* point in the same direction. If we plot the velocity of halogenation of acetone as a function of p_H, the curve has a minimum at $p_H = 4$.[18] In the case of bromoacetones, this minimum occurs at lower p_H values. As a result the minimum for highly brominated acetones in mixtures of water and acetic acid (1 : 1) containing HCl is shifted beyond 1 normal HCl concentration. Monobromacetone shows a minimum between 10^{-2} and 10^{-3} n HCl concentration. Assuming the acetate ion to be the catalyzing base and considering the fact that the minimum velocities in the case of acetone and monobromoacetone are not very different, one can deduce, that the basic catalysis is increased by a factor

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[15] J. Hochberg, unpublished.

[16] B. Eistert, *Tautomerie and Mesomerie* (Enke, Stuttgart, 1938).

* J. Horiuti and Y. Sakamoto found a slow exchange in chloroform, when treated at 100° with 2.5 volume percent of $0.1n$ KOD solution. (Bull. chem. Soc. Jap. **11**, 627 (1936). They announced a further publication which will perhaps allow the calculation of the velocity constants of the reaction.

[17] H. B. Watson and E. D. Yates, J. Chem. Soc. London 1207 (1932).

[18] H. M. Dawson and N. C. Dean, J. Chem. Soc. 2875 (1926).

of 10 or 100 as the result of substitution by one bromine atom.

We may therefore conclude that also in the case of the OH⁻ ion as catalyst the velocity of ionization is increased by halogen substitution. The OH⁻ catalyzed bromination of acetone should therefore immediately give a tribromoacetone. It was shown above that this gives an explanation for the difference observed between the exchange and bromination velocities of acetone. In the case of acid catalysts monobromoacetone is brominated more slowly than acetone, so that monobromoacetone is first formed. This agrees with the general experience that the same substituents have an opposite effect in acid and base catalysis.[19]

The halogens are typical representatives of the so-called "negative" substituents. Their influence is due to an "inductive effect" and must not be confused with the "electromeric" effects of substituents such as NO_2, CO, etc. It is generally assumed that this inductive effect is due to the tendency of a halogen atom, to attract electrons. The bromination experiments show, that this tendency is transmitted to the carbon atom, with which the halogen atom is linked. Hydrogen atoms, attached to the carbon atom, become in this way removable as protons. The bromination experiments conflict with the opposite idea that the carbon atom, acquires a tendency to repell electrons as a result of halogen substitution. According to this theory of the "disintegrated octet" the removal of the hydrogen atoms as protons should become more difficult.

8. Hydroxyl Compounds

The introduction of a hydroxyl group at a carbon atom attached to ionizable H atoms produces the inverse effect to that of an halogen atom. The tendency for CH to ionize is decreased. This was shown in experiments using alkaline solutions of *glycollic acid*.[20] The velocity constant of CH ionization in the glycollate ion at 137°C for $1n$ OD⁻ concentration was found to be $\sim 5 \cdot 10^{-3}$ min.⁻¹; while the corresponding velocity constant of the acetate ion is $3.7 \cdot 10^{-2}$ min.⁻¹. The ionization velocity of the hydroxylated

compound is about 1/7 that of the unsubstituted compound, at 137°C. Assuming that the difference is caused by a difference of activation energy, the factor becomes about 1/10 at room temperature. Therefore we may take the rate constant of the glycollate ion to be $\sim 1 \cdot 10^{-7}$ at 25°C.

Qualitatively we find a similar decrease when we compare the ionization velocity of *dihydroxyacetone* with that of acetone.[11] The ionization velocity of dihydroxyacetone can be deduced employing the same assumption as with acetaldehyde. A 1 : 1 mixture of dihydroxyacetone and glyceraldehyde in a sufficiently diluted alkali solution gives a straight aldol condensation forming fructose and sorbose. If the condensation is carried out in heavy water, no deuterium is found in the CH linkages of the sugar. Therefore the velocity of condensation should be equal to the ionization rate of dihydroxyacetone. The rate constant of the condensation reaction has not yet been measured, but we know that the reaction is complete in about 40 minutes in $0.02n$ alkaline solution. If we assume that this means that 90 to 99 percent of the condensation is finished in this time, we obtain $k \sim 5$ min.⁻¹ at $1n$ OD⁻ concentration. This must be compared with the value of k for acetone 14.5. We find again a decrease of velocity, caused by the substitution of two hydrogen atoms by hydroxyl groups. The difference seems to be smaller than in the case of acetic acid.

Glyceraldehyde alone gives fructose and sorbose as condensation products in alkaline solution; the velocity of the reaction is about three times smaller than in the presence of dihydroxyacetone. We may consider the ionization at the α carbon atom of glyceraldehyde to be the rate determining step.[11] This gives a value between 1 and 2 min.⁻¹ for k under conditions corresponding to the above. The rate is 5–10 times slower than that of acetaldehyde. The rates cannot be compared directly since we have a substitution by a hydroxyl group and a hydroxymethyl group at the same time. As it will be shown in the next section that a methyl group also decreases the tendency to CH ionization, this result is not unreasonable.

The fact, that an OH substitution decreases the tendency to ionization, is unexpected. Having

[19] H. B. Watson, *Modern Theories of Organic Chemistry* (Oxford, 1937); C. K. Ingold, J. Chem. Soc. London 1032 (1930).
[20] K. H. Geib, unpublished.

TABLE I. *Velocity constants of CH ionization in aqueous solutions (k given in min.⁻¹ at constant base concentration and at 25°C, calculated with natural logarithms).*

| COMPOUNDS | CATALYZING BASE | | | REFERENCES |
	OD⁻ ION 1n	ACETATE ION 1n IN H_2O	$H_2O(c = 55.5)$	
Nitromethane	$\sim 2 \cdot 10^3$	$4.5 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	4 5 6 7
Monobromonitromethane	—	—	$8 \cdot 10^{-4}$	6
Nitroethane	$3.3 \cdot 10^2$	—	—	4 6
Acetone	14.5	$1.5 \cdot 10^{-5}$	$5 \cdot 10^{-10}$	8 10 22
Monobromoacetone	—	$\gg 1.5 \cdot 10^{-5}$	—	17
Dihydroxyacetone	~ 5	—	—	11
Acetaldehyde	11	—	—	11 12
Glyceraldehyde	1–2	—	—	11
Acetonitrile	$2-3 \cdot 10^{-3}$	—	—	14
Acetamide	$\sim 1 \cdot 10^{-3}$	—	—	14
[Acetic acid, undiss.]	$[\sim 10^{-2}]$	—	—	13
Acetate ion	$\sim 1 \cdot 10^{-6}$	—	—	13
Glycollate ion	$1 \cdot 10^{-7}$	—	—	20
Methylsulfonic acid (ion)	$\sim 2 \cdot 10^{-7}$	—	—	15

regard to the electron affinity of the O atom we would expect the effect of OH to be similar to that of halogens. The experiment appears to show that, besides the "inductive" influence of a substituent, there is yet another influence operative, affecting the atoms in the immediate neighborhood. It is possible that this effect is a steric one, but it is also possible that it depends upon the protophilic nature of the OH⁻ ion. It may be that this ion sometimes removes a proton from the hydroxyl substituent instead of from a carbon atom and that it is thereby made ineffective.

9. ALKYL GROUPS

The influence of alkyl groups has been measured directly by Maron and La Mer[4] in their investigation of the nitroparaffins. They found the following neutralization velocity constants at 0°C in water.

Nitromethane	Nitroethane	Nitroisopropane
237.6	39.11	2.08 min.⁻¹

whereas Junell using the bromination method found the constants

Nitroethane	Nitropropane
35.2	29.2 min.⁻¹.

This shows that the substitution by alkyl groups decreases the tendency to CH ionization at the α carbon atom.

This result agrees with the experiments of Ives,[21] who showed that the deuterium exchange in propionate ions is about 15 times slower than the exchange in acetate ions at 100°C.

SUMMARY

We summarize our results in Table I in which the data dealt with in this paper are collected. The values of the first column vary between 10^{+3} to 10^{-7}. The advantage of having many comparable values can be obtained only at the expense of the accuracy of some of the figures.

We can state the following order: $NO_2 \cdots CO \cdots CN, CONH_2, \cdots COO^-, SO_3^- \cdots Cl, (OH, CH_3)$ in which the substituents taken from left to right increase the tendency to CH ionization. The substituents in parenthesis have a decreasing effect.

²¹ D. J. G. Ives, J. Chem. Soc. London 81 (1938).
²² G. F. Smith, J. Chem. Soc. London 1744 (1934).