CXIII.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures.*

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IN a previous paper (T., 1914, 105, 1260) the author recorded some experiments on the inversion of sucrose by acids in water-ethyl alcohol mixtures. It was there found that the rate of inversion at first decreased slightly as water was replaced by alcohol up to about 50 per cent. of alcohol, and then increased. It was concluded from the results that the catalytic activity of the acid was really greater in alcohol than in water, and that the addition of water had a depressing effect on the rate of hydrolysis. At the same time, the author was unable to explain the decrease in the rate of inversion which results from the replacement of water by alcohol up to 50 per cent. mixtures without assuming that the mixed solvents had some specific effect on the rate of reaction, and it was there suggested that this was due to a change in the fluidity of such mixtures, causing a variation in the rate of catalysis similar to that observed in conductivity.

In obtaining the results in that work, the reaction was treated as a unimolecular one, the concentration of the water being neglected. This assumption was made in view of the fact that even in a solution containing 75 per cent. of alcohol by volume the ratio of the number of molecules of water to molecules of sugar present at the commencement of the reaction was 45, so that the decrease in concentration of the water during the reaction was only $1/45$ of its original value. In a 50 per cent alcohol mixture the ratio was 91. Under these conditions, it was considered that the concentration of the water could be omitted from the equation and the reaction considered as unimolecular.

If, however, the concentration of the water is considered, the value of k_1 , calculated from the bimolecular equation

$$k_1 = \frac{1}{t(w-b)} \log \frac{b(w-x)}{w(b-x)}$$

(where b and w are the number of gram-molecules of sugar and water respectively in the solution at the beginning of the reaction), is, of course, much smaller than the corresponding value of k obtained from

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

In this case, the total concentration of water is considered to represent its mass as one of the active substances, irrespective of the fact that it is present in large excess and only a small fraction of the total concentration is used up during the reaction.

The difference between the values of k and k_1 is shown in the following table:

Sucrose (10 per cent.) and N/2-Hydrochloric Acid at 25.0°.

Alcohol (volume per cent.).	k .	k_1 .
0.0	0.00219	0.0000427
16.7	0.00213	0.0000491
25.0	0.00204	0.0000519
40.0	0.00192	0.0000607
50.0	0.00176	0.0000667
60.0	0.00185	0.0000877
75.0	0.00208	0.0001603

It will be seen that whereas the values of k pass through a minimum for a certain mixture, the values of k_1 steadily increase.

It appeared of interest to see if similar results would be obtained in the case of ester hydrolysis, and with this end in view experiments have since been performed on the rate of hydrolysis of methyl acetate by hydrochloric acid. Owing to its effect on the equilibrium, alcohol could not be used as one of the solvents in this research, so that the experiments were performed in mixtures of acetone and water. Acetone undergoes change under the influence of the acid used in the hydrolysis, but it has been assumed that this has no effect on the rate of hydrolysis of the methyl acetate.

The acetone used in these experiments was dried over and distilled from calcium chloride. The methyl acetate was freed from acetic acid by means of sodium carbonate and was distilled from calcium chloride; it was neutral to litmus. The volume of the

1232 BURROWS: THE RATE OF HYDROLYSIS OF METHYL

solution was adjusted at the temperature of the experiment, which was 25° in every case. The acetone percentages given are by volume; thus 70 per cent. acetone was prepared by mixing seven volumes of acetone with three of water. In preparing a 5 per cent. solution of methyl acetate for hydrolysis by *N*/2-hydrochloric acid in 70 per cent. acetone, the following method was adopted: 10 c.c. of methyl acetate were diluted to 100 c.c. at 25° with 70 per cent. acetone (*A*), 20 c.c. of 5*N*-hydrochloric acid were mixed with 46.7 c.c. of anhydrous acetone, and the mixture was diluted to 100 c.c. at 25° with 70 per cent. acetone (*B*). Equal volumes of (*A*) and (*B*) were then mixed in a dry flask and placed in a thermostat at 25°. The weights of water and acetone used in preparing the solutions were also determined, so that all concentrations can be expressed in terms of gram-molecular weights. The reaction was followed in the usual way by titrating 5 c.c. of the solution under investigation with baryta solution after different intervals of time, the increase in titre indicating the concentration of the acetic acid produced. At first the reaction was treated as unimolecular, and the values of *k* were calculated from the equation

$$k = \frac{1}{t \sqrt{4bn+1}} \log \frac{4bn+2nx(\sqrt{4bn+1}-1)}{4bn-2nx(\sqrt{4bn+1}+1)} \quad (1)$$

obtained by integrating $\frac{dx}{dt} = k(b-x) - k_2x^2$.

In this equation $n = \frac{b-\xi}{\xi^2}$, where ξ represents the amount of ester which actually undergoes hydrolysis up to the equilibrium, *b* is the initial concentration of ester, and *x* the amount hydrolysed in time *t*. It was found that the above equation gave values of *k* which were quite constant for any particular solution. However, in the case of a series of experiments in different water-acetone mixtures, it was found that as the water was replaced by acetone the value of *k* at first decreased and then increased.

Owing to the relatively small concentration of water in solutions containing a high percentage of acetone, it was then decided to calculate all results also from the equation for a bimolecular reaction. The equation used was that given by Griffith and Lewis (T., 1916, 109, 69),

$$k_1 = \frac{1}{tA} \log \frac{A+y+2(K-1)x}{A-y-2(K-1)x} \cdot \frac{A-y}{A+y} \quad (2)$$

obtained by integrating $\frac{dx}{dt} = k_1(b-x)(w-x) - k_2x^2$,

where

k_1 = rate of hydrolysis,

k_2 = rate of esterification,

b = initial number of gram-molecules of methyl acetate in 1000 c.c. of solution,

w = initial number of gram-molecules of water,

x = number of molecules of ester decomposed in time t .

In equation (2),

$$y = (w + b)$$

$$A = \sqrt{(w + b)^2 + 4(K - 1)wb}$$

and
$$K = \frac{k_2}{k_1} = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}} \text{ at equilibrium.}$$

The values of both k and k_1 obtained in any solution were found to be constant. This is seen in tables I and II, which contain the results for the hydrolysis of 5 per cent. methyl acetate by $N/2$ -hydrochloric acid in 80 and 90 per cent. acetone (by volume) respectively.

TABLE I.

80 Per cent. Acetone.

$$b = 0.6267; w = 10.20; K = 5.14.$$

t .	x .	$k_1 \times 10^5$.	$k \times 10^4$.
0	—	—	—
48.5	0.0506	7.41	7.51
78.5	0.0819	7.44	7.79
111	0.1095	7.43	7.56
138	0.1314	7.34	7.44
168	0.1575	7.44	7.55
228	0.1992	7.32	7.40
258	0.2200	7.36	7.43
318	0.2592	7.47	7.52
401	0.2983	7.31	7.35
∞	0.4963		
Mean ...		7.40	Mean 7.51

TABLE II.

90 Per cent. Acetone.

$$b = 0.6267; w = 4.752; K = 8.97.$$

t .	x .	$k_1 \times 10^5$.	$k \times 10^4$.
0	—	—	—
50	0.0636	19.77	9.35
85	0.0991	18.95	8.91
10	0.1262	19.35	9.08
140	0.1523	19.12	8.94
206	0.2018	18.91	8.80
263	0.2435	19.80	9.18
324	0.2695	19.34	8.94
400	0.2957	19.16	8.82
484	0.3192	19.63	9.00
∞	0.3608	—	—
Mean ...		19.56	Mean 9.00

1234 BURROWS: THE RATE OF HYDROLYSIS OF METHYL

In table III is given a summary of results obtained for the hydrolysis of 5 per cent. methyl acetate by $N/2$ -hydrochloric acid in different water-acetone mixtures. The value of b is 0.6267 in each case. The value of K was determined by ascertaining at the completion of the reaction the amount of acetic acid produced and then calculating the equilibrium constant. It was found that the numbers so obtained varied with the different solutions. This method of determining the conditions at equilibrium by analysing the solution actually used for the rate of hydrolysis is undoubtedly open to error, as a small amount of the volatile substances must escape each time the flask is opened to determine the concentration of acetic acid at each particular time. The amount lost in this way during a complete experiment would probably be sufficient to introduce an error into the value of C (acetic acid), and this might lead to quite a large error in the value of K . The variations in K are possibly due to a small error in the values of the concentrations of acetic acid found for the various solutions. At the same time, it has been found that a comparatively large difference in K produces only a small difference in the value of k_1 . Thus the mean value of k_1 for a solution containing 90 per cent. of acetone is found to be 19.56 when $K=8.97$ and 18.7 when K is taken as 5, the approximate value found in the other solutions.

In the latter case, however, the numbers obtained for k_1 decrease regularly, whereas if the experimental values of K are taken there is no such decrease. For this reason, it has been decided to employ the values of K actually found, although it is realised that the variation in its value for the different solutions may be due, in part at least, to the method of determination.

In the following table, the values under k are calculated from equation (1), those under k_1 from equation (2).

TABLE III.

Methyl Acetate (5 per cent.) and N/2-Hydrochloric Acid.

Acetone (volume per cent.).	Gram-molecules of acetone per litre.	w .	K .	$k_1 \times 10^5$.	$k \times 10^4$.
0	0	52.32	5.40	2.76	13.58
20	2.665	42.46	5.10	3.03	12.28
40	5.39	32.08	4.38	3.38	10.33
60	8.10	21.23	4.47	3.86	7.91
70	9.42	15.72	4.51	4.56	7.05
80	10.66	10.20	5.14	7.40	7.51
90	11.84	4.752	8.97	19.56	9.00

It will be seen that the value of k_1 increases regularly as water is replaced by acetone as solvent. The values in the sixth column

under k , however, at first decrease as water is replaced by acetone and then increase.

A similar result was obtained for the hydrolysis of 2.5 per cent. methyl acetate by $N/10$ -hydrochloric acid. Owing to the small amount of methyl acetate actually present at equilibrium, the value taken for K for each of the solutions in this series was the value found in the corresponding solution with 5 per cent. methyl acetate and $N/2$ -hydrochloric acid.

TABLE IV.

Methyl Acetate (2.5 per cent.) and N/10-Hydrochloric Acid.

In all cases, $b = 0.3133$ gram-molecules per litre.

Acetone. Per cent.	Gram-molecules of acetone.	w .	$k_1 \times 10^4$.	$k \times 10^4$.
0	0	54.00	4.78	2.60
20	2.73	43.97	5.40	2.39
40	5.53	33.44	5.76	1.90
60	8.31	22.26	6.40	1.42
70	9.68	16.62	7.42	1.22
80	10.96	10.95	10.23	1.13
90	12.19	5.351	23.60	1.26

Discussion of Results.

If the values of k_1 given in tables III and IV are plotted against water concentrations, they are found to lie on a rectangular hyperbola. In the accompanying diagram, a graph is also shown for the results obtained for sucrose inversion given under k_1 in the table at the beginning of this paper. It will be seen that the three curves are similar in shape and indicate the decrease in catalytic activity of the acid which accompanies an increase in the water concentration.

Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 253), Acree (*Amer. Chem. J.*, 1912, **48**, 352), and Taylor (*Zeitsch. Elektrochem.*, 1914, **20**, 201) have advanced the theory that the undissociated molecule of the acid also acts as a catalyst, the activity of the undissociated molecule of hydrochloric acid varying for different reactions up to a value twice that of the hydrogen ion. In order to account for the present results according to this theory, it would be necessary to assume that $\frac{k_m}{k_H}$ is about 20 (k_m being the activity of the undissociated molecule and k_H that of the hydrogen ion). Figures are not available for the degree of dissociation of hydrochloric acid in water-acetone mixtures, but in discussing the results obtained for the inversion of sucrose (*loc. cit.*), the author

1236 BURROWS: THE RATE OF HYDROLYSIS OF METHYL

gave values of a (HCl) deduced for water-alcohol mixtures. In the following table, the values observed for k_1 for sucrose inversion

- (a) Inversion of sucrose in water-alcohol.
 (b) Hydrolysis of methyl acetate ($N/10\text{-HCl}$) in acetone-water
 (c) " " " ($N/2\text{-HCl}$) " " "

(calculated as a bimolecular reaction) are compared with the total catalytic activity of the acid expressed as

$$k_m + k_H = k_H[a + 20(1 - a)],$$

the ratio $\frac{k_m}{k}$ being taken as 20.

TABLE V.

Alcohol (volume per cent.).	α (HCl).	$[\alpha + 20(1 - \alpha)]$.	$k_1 \times 10^5$.	$\frac{k_1 \times 10^5}{[\alpha + 20(1 - \alpha)]}$.
0	0.86	3.66	4.27	1.17
25	0.83	4.23	5.19	1.23
40	0.80	4.80	6.07	1.26
50	0.72	6.32	6.67	1.06
60	0.65	7.65	8.77	1.15
75	0.45	11.45	16.03	1.11

The numbers in the fifth column approximate to a constant. Although results cannot be calculated in this way for the hydrolysis of methyl acetate in water-acetone mixtures owing to lack of data, it is considered from the results obtained for k_1 in these solutions that if the value of α (HCl) were available, a similar constancy for $\frac{k_1}{a + x(1 - a)}$ would be obtained for a value of x in the neighbourhood of 20.

It follows from the above that the activity of the catalyst in these mixtures can best be expressed by $k_1 = k_m + k_H$, when the ratio $\frac{k_m}{k_H}$ is considered to be about 20, but this value is not supported by results obtained by Snethlage and others for the catalytic effect of hydrochloric acid in other reactions.

The shape of the curves in the diagram suggests that in the mixtures investigated the variation of the activity of the acid with the water content is approximately expressed by $k_1(w + m) = n$, where m and n are constants and k_1 the observed rate of hydrolysis in a solution containing w gram-molecules of water. An equation of this type is capable of various interpretations, but taken in conjunction with the marked decrease in k_1 with increase in water concentration for low values of the latter, it indicates that the water plays a very markedly anticatalytic rôle compared with the other constituents of the solution, that is, the value of the constant m must be very small compared with w . This may be interpreted (compare Lapworth and Fitzgerald, T., 1908, 93, 2168) as being due to the conversion of active, free hydrogen ions to inactive ions by the solvent, the effect of the water in this respect being far greater than that of the acetone. Or it may be interpreted as indicating that the reactive substance in ester hydrolysis is a complex between the ester and water, which is readily dissociated by the excess of water in the solution (Griffiths and Lewis, *loc. cit.*). It may also be interpreted as representing the dissociating effect of the solvent on a complex between the ester and the catalyst, which is considered to be the reactive

1238 THE RATE OF HYDROLYSIS OF METHYL ACETATE, ETC.

substance. Such a complex may either be dissociated by the solvent into the original substances or else hydrolysed by the water into the final products of hydrolysis. For the concentrations usually employed in hydrolysis the amount of this complex is very small owing to the high dissociating power of the water. As the latter is replaced by acetone or other liquid the dissociating power of the medium is decreased and the concentration of the complex is increased, so that the observed rate of hydrolysis is also increased. In any of the above cases it is possible to assign a small value to the term m , which really represents the relatively small power of the other constituents of the solution of converting an active substance into one which is inactive in catalysis. The following discussion is independent of the nature of m ; it is concerned rather with its magnitude. We will assume that it is simply a function of the concentration of the other variable in the solution, namely, acetone. If we substitute in the equation $k_1(w+m)=n$ the values of k_1 and w in table III for solutions containing (a) 52.32 gram-molecules of water and no acetone, and (b) 4.752 gram-molecules of water and 11.84 of acetone, we obtain the value $m=0.22$ (in terms of 1 gram-molecule of acetone in the solution). Substituting this value for the other solutions, the following results are obtained.

TABLE VI.

Acetone.	Acetone $\times 0.22$	w .	$k_1 \times 10^5$.	$n = k_1(w + 0.22 \times \text{acetone})$.
0.0	—	52.32	2.76	144
2.665	0.59	42.46	3.03	130
5.39	1.19	32.08	3.38	112
8.10	1.78	21.23	3.86	89
9.42	2.07	15.72	4.56	81
10.66	2.35	10.20	7.40	93
11.84	2.60	4.752	19.56	144

The numbers in the last column pass through a minimum value, and vary in a similar manner to the values under k in table III. Furthermore, for any small value of m in the equation $k_1(w+m)=n$, the values of n will be found to vary as in table VI. The similarity between the variations of k in table III and n in table VI appears to justify the use of the equation for a unimolecular reaction in mixtures such as those used in this work, in which the total concentration of water varies considerably in the different solutions. It would appear that any specific effect of the solvent on the rate of hydrolysis, other than that due to its dissociating power, is more directly shown by disregarding the change in the concentration of the water in the different solutions. It is considered that the minimum value obtained for k (or n) has a definite meaning. It is interpreted as indicating a specific influence of these mixtures on the rate of catalysis, similar to that

observed in the conductivity of certain electrolytes dissolved in them, or in the fluidity of the mixtures themselves. The solution of either alcohol or acetone in water is accompanied by contraction, and it is considered that the condensed state of such a mixture has a retarding influence on catalysis.

Summary.

The rates of hydrolysis of methyl acetate by $N/2$ - and $N/10$ -hydrochloric acid have been measured in various water-acetone mixtures. The velocity constants have been calculated according to both unimolecular and bimolecular equations, the reverse reactions being considered in both cases.

It has been found that if the total water concentration is taken as representing its active mass, then the rate of hydrolysis increases as water is decreased in the mixtures throughout the series. The results obtained approximate to $k_1 = k_m + k_H$ if $\frac{k_m}{k_H}$ is taken as 20 (approximately). The variation of k_1 with water concentration indicates the anticatalytic function of the latter, and if the values of k_1 are corrected for this effect the numbers so obtained are found to vary in a manner similar to those obtained by using the ordinary unimolecular equation, and pass through a minimum value for a certain mixture. This minimum is considered to have a definite meaning, representing a retarding influence of such mixtures on catalytic reactions.

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[Received, August 23rd, 1919.]