CCLXXXII.—*Acid and Salt Effects in Catalysed Reactions. Part XV. The Catalytic Activity of Hydrochloric Acid in the Hydrolysis of Ethyl Acetate.*

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THE experiments to be described in this paper represent an attempt to measure as accurately as possible the catalytic effect produced by hydrochloric acid of widely varying concentration in the hydrolysis of ethyl acetate.

If the active mass of the hydrolyte is constant and the catalytic effect is assumed to be due to the hydrogen ion, then according to the classical theory the reaction velocity should be given by the equation $v = kc_H$. On the other hand, the equation for the velocity according to the activity theory is $v = k'a_H = k'f_H . c_H$ in which the activity coefficient f_H varies with the hydrogen-ion concentration, or, more generally, with the ionic concentration of the reaction medium.

According to Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169; 1925, **115**, 337), these equations are particular forms of a more general equation, for the applicability of which a substantial amount of experimental evidence has been brought forward. In terms of this equation, the influence of the ionic environment which is expressed by f_H depends on the nature of the primary reaction. If this involves the interaction of the hydrogen ion with a neutral molecule, the reaction velocity should not be greatly affected by the ionic concentration of the reaction medium, but the converse would be true if the primary change involves the interaction of the hydrogen ion with a negatively charged entity.

For certain reactions, it may not be difficult to identify with some degree of certainty the constituents which are involved in the primary change, but this is by no means generally the case. In such circumstances it cannot be definitely stated whether a given reaction will or will not be markedly affected by variations in the ionic environment. This, indeed, is a matter for experiment, and in the consideration of the data yielded by experiments on acid-catalysed reactions it is of the first importance to ascertain whether the observed catalytic effect is simple or composite. This necessitates the consideration of the effects which may be produced by neutral molecules and negative ions, as well as those which are due to the " hydrogen " or other similar positive ions. Unless due regard is paid to the possibility of such simultaneous catalytic effects, it is scarcely feasible to discuss the question whether the catalytic activity of the hydrogen ion is proportional to its concentration, or whether it is dependent on a factor which varies very appreciably with the ionic concentration of the reaction medium. Furthermore, since the ionisation constants of weak acids are changed by the addition of catalytically inert salts, it is obvious that any attempt to discriminate between concentration and " activity " as the factor which determines the catalysing power of the hydrogen ion requires a careful choice of the experimental conditions. These should be such that the observed catalytic effect can with reasonable certainty be ascribed entirely to the hydrogen ion, and it should further be possible to measure the reaction velocity over a wide range of hydrogen-ion concentrations, for which range the corresponding variations in the thermodynamic activity should be known with some degree of certainty.

These considerations suggested hydrochloric acid as a suitable catalyst for investigation, for, on the one hand, there is good reason to suppose that this acid is almost completely ionised in dilute solution and that the catalytic effects produced by it may be ascribed entirely to the hydrogen ion, and, on the other, the dependence of the thermodynamic activity of hydrochloric acid on its concentration has been determined with considerable precision by various methods.

In selecting the hydrolysis of ethyl acetate as an acid-catalysed reaction for which the requisite conditions would appear to be satisfied, we were also influenced by the circumstance that this reaction had been previously studied with results which were said to support the view that the catalytic effects produced by hydrochloric acid are related to the thermodynamic activity of the hydrogen ion.

The data recorded by Harned and Pfanstiel (*J. Amer. Chem. Soc.*, 1922, **44**, 2193) suggest that the specific catalytic activity of hydrochloric acid passes through a minimum at a concentration of 0·07—0·08 mol. per litre. This minimum is supposed to be connected with a minimum in the activity coefficient of the hydrogen ion, which according to these authors occurs at an acid concentration of 0·15—0·18 mol. per litre.

From a study of the effects produced by the addition of chlorides to a 0·05*N*-hydrochloric acid solution, Åkerlöf (*Z. physikal. Chem.*, 1921, **98**, 260) draws the conclusion that the catalytic activity of the acid is proportional to the cube root of the activity of the hydrogen ion. Such a relation can scarcely be regarded as other than empirical. For other reactions, *e.g.*, the inversion of sucrose (compare Jones and Lewis, J., 1920, **117**, 1120; Moran and Lewis, *ibid.*, 1922, **121**, 1613; Scatchard, *J. Amer. Chem. Soc.*, 1921, **43**, 2387), where the experimental results have been interpreted in terms of the activity of the hydrogen ion, the proof of the alleged relation between reaction velocity and hydrogen-ion activity appears to be equally inconclusive. The conversion of *N*-chloroacetanilide into *p*-chloroacetanilide in presence of hydrochloric acid (compare Harned and Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475; Soper and Pryde, J., 1927, 2761) is not catalysed by hydrogen ions and will not therefore be discussed here.

The evidence for the view that the rate of hydrolysis of ethyl acetate with hydrochloric acid as catalyst is determined by the thermodynamic activity of the hydrogen ion did not seem to us to be acceptable, and for this reason new measurements have been undertaken which extend the previous lower limit for the concentration of the hydrochloric acid from 0·01*N* (compare Taylor, *Medd. K. Vetenskapsakad. Nobel.-Inst.*, 1913, **2**, No. 34; Harned and Pfanstiel, *loc. cit.*) to the much lower value 0·0002*N*.

When the concentration of the hydrochloric acid is less than 0·01*N*, the course of the reaction is markedly affected by the acetic acid produced. This autocatalytic influence of the acetic acid, which increases as the concentration of the hydrochloric acid diminishes, precludes the use of any simple integration formula in the co-ordination of the experimental data. We have therefore attempted to measure directly the velocity of the reaction in the early stages of hydrolysis. These measurements were made at

25° with a fixed concentration of ethyl acetate ($e = 0{\cdot}206$ mol. per litre) in presence of hydrochloric acid varying in concentration from $c = 0{\cdot}0002$ to $c = 0{\cdot}002$ mol. per litre. Carefully selected, chemically inert flasks were used as containers.

In these experiments, the reaction was allowed to proceed until a small proportion (0·5—3%) of the ester was hydrolysed. If Δx denotes the concentration of the acetic acid formed during the interval t, then $\bar{v} = \Delta x/t$ represents the mean velocity for this period, and $x = \Delta x/2$ is the mean concentration of the acetic acid. For the attainment of the primary object of these experiments it was soon realised that the values of x which determine the magnitude of the autocatalytic effect must be kept as small as possible, and this necessitated the carrying out of the observations on a large scale which may be illustrated by reference to the detailed procedure followed in an experiment with 0·0005*N*-hydrochloric acid. The requisite amount of a 0·01*N*-hydrochloric acid solution was weighed into a 250 c.c. flask, and freshly distilled water was added to give about 240 c.c. of solution. When the temperature had reached 25°, 5·00 c.c. of ester were added and the volume was made up to 250 c.c. After a suitable interval (about 4 days) the entire contents of the flask were titrated with 0·1*N*-sodium hydroxide solution. The initial acidity was derived from the immediate titration of a similarly prepared parallel solution. For $t = 5864$ minutes, the titration difference thus obtained was 10·83 c.c., which represents 2·1% hydrolysis and corresponds with $\Delta x = 0{\cdot}00433$, $x = 0{\cdot}00216$, and $\bar{v} = 7{\cdot}38 \times 10^{-7}$ mol. per litre per minute.

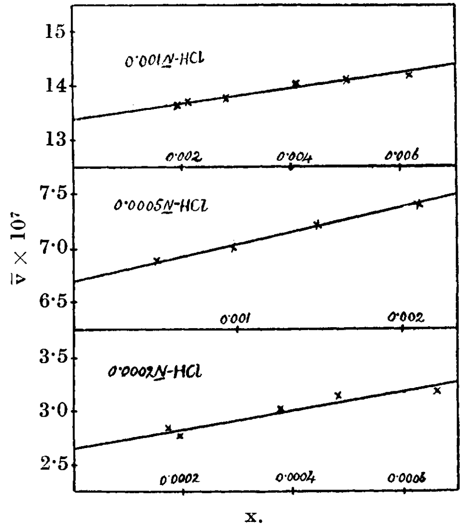
If for small values of x, the magnitude of which depends on the concentration (c) of the hydrochloric acid, the observed mean reaction velocities ($\bar{v}$) are plotted against the corresponding mean acetic acid concentrations (x), a straight line is obtained. By extrapolation to $x = 0$, the autocatalytic effect may be eliminated, and the initial velocity v_0 due to the undisturbed action of the hydrochloric acid may be derived. Since the mean ester concentration $(e - x)$ falls slightly as x increases, more strictly comparable velocities are those given by $\bar{v}' = \bar{v}e/(e - x)$, but as a matter of fact the substitution of $\bar{v}'$ for $\bar{v}$ makes no appreciable difference to the value of the extrapolated initial velocity. The graphs of $\bar{v}$ against x are shown in Fig. 1, and the initial velocities derived from these are $v_0 = 13{\cdot}40 \times 10^{-7}$, $6{\cdot}70 \times 10^{-7}$, and $2{\cdot}65 \times 10^{-7}$ respectively for $c = 0{\cdot}001$, $0{\cdot}0005$, and $0{\cdot}0002$ mol. per litre. From these initial velocities, the values of the catalytic coefficient k are then given by $k = v_0/ce$.

As the concentration of the hydrochloric acid increases, the autocatalytic influence of the acetic acid diminishes rapidly. For

$0{\cdot}002N$-hydrochloric acid, the autocatalytic effect is almost exactly counterbalanced by the effect of the fall in the ester concentration, with the result that the observed mean velocity in the early stages of hydrolysis is practically identical with the initial velocity.

In hydrochloric acid solutions more concentrated than $0{\cdot}01N$, the autocatalytic effect may be almost entirely neglected in comparison with the change in the velocity which is due to the fall in the ester concentration, and for these solutions the velocity coefficient has been derived from the formula $k = 1/ct \,.\, \log e/(e - \Delta x)$, having due regard for the range over which this is applicable without appreciable interference from the reverse reaction (compare Dawson and Lowson, J., 1927, 2107).

FIG. 1.



Plot of mean reaction velocity ($\bar{v}$) *against mean acetic acid concentration* (x) *for* 0·001N-, 0·0005N-, *and* 0·0002N-*hydrochloric acid as catalyst.*

The values of k obtained by the above methods are in Table I.

TABLE I.

c	0·0002	0·0005	0·001	0·002	0·01	0·02	0·04	0·1	0·2	0·5
$k \,.\, 10^3$	6·43	6·50	6·50	6·49	6·54	6·45	6·50	6·48	6·57	6·76

In the consideration of these figures, it may be noted that $c = 0{\cdot}0002$ represents the lowest concentration of hydrochloric acid for which it is possible in practice to make use of the linear extrapolation method. At greater dilutions, the autocatalytic effect plays too large a part. For the interval $c = 0{\cdot}0002$—$0{\cdot}2$, the constancy of k, within the limits of experimental error, signifies that the catalytic activity of the hydrochloric acid is proportional to its concentration. Over this range the activity coefficient falls from 0·994 to 0·783 (Lewis and Randall, " Thermodynamics ") and the mean activity coefficient from 0·997 to 0·884. According to Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1818), the fall in the individual activity coefficient of the hydrogen ion is less than this, but the argument on which this conclusion is based seems doubtful. In the circumstances, the mean activity coefficient would seem to afford the only data for comparing the activity and the concentration of the hydrogen ion, and as is evident from the constancy of k in the above table, there is no apparent connexion between the catalytic activity and the thermodynamic activity.

The fact that k increases with c at higher concentrations (compare, *e.g.*, Harned and Pfanstiel, *loc. cit.*) may be due to the action of undissociated hydrochloric acid, which is in all probability a very active catalyst. Ionic effects of the kind associated with catalytically inert salts (compare Dawson and Key, this vol., p. 1239) may also play a part, and it does not yet seem possible to attempt the interpretation of the observations which have been made on the action of hydrochloric acid in concentrated solutions.

The mean reaction velocities used in the above-described method for the elimination of the autocatalytic effect represent only a part of the observations made with dilute hydrochloric acid solutions. Other measurements were made in which the proportion of acetic acid was greater, and prior to the consideration of the experimental data, the catalytic process may be subjected to closer analysis.

In accordance with previous results, the equation for the reaction velocity may be written

$$\begin{aligned} v &= v_h + v_{\mathrm{OH}} + v_a + v_w + v_m \\ &= \{k_h[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + k_a[\mathrm{A}^-] + k_w[\mathrm{H_2O}] + \\ &\qquad k_m[\mathrm{HA}]\}\,.\,[\text{ester}][\text{water}] \quad . \quad (1) \end{aligned}$$

Since $k_{\mathrm{OH}}/k_h = 10^3$, it follows that the v_{OH} term may be neglected if the hydrogen-ion concentration is greater than 10^{-4}. This was actually the case in all experiments. From the ratios $k_a/k_h = 3{\cdot}3 \times 10^{-5}$ and $k_m/k_h = 2{\cdot}4 \times 10^{-4}$ (Dawson and Lowson, J., 1927, 2444) it is also apparent that v_a and v_m may be neglected in comparison with v_h. The term v_w is probably extremely small, evidence for this view being afforded by the reaction-velocity data for mixtures of the series $0{\cdot}1\mathrm{CH_3{\cdot}CO_2H} + x\mathrm{CH_3{\cdot}CO_2Na}$, which can be satisfactorily interpreted without the introduction of such a term. It would therefore appear that the velocity of hydrolysis under the conditions of these experiments is determined by the concentration of the hydrogen ion. We may therefore write

$$v = k_h[\mathrm{H}^+][\text{ester}][\text{water}] = k[\mathrm{H}^+][\text{ester}] \quad . \quad . \quad (2)$$

Furthermore, since $[\mathrm{H}^+] = [\mathrm{Cl}^-] + [\mathrm{A}^-] = c + [\mathrm{A}^-]$

and $[\mathrm{A}^-] = K(x - [\mathrm{A}^-])/(c + [\mathrm{A}^-])$

we derive $[\mathrm{H}^+] = c + \frac{1}{2}\{\sqrt{(K+c)^2 + 4Kx} - (K+c)\}$ (3)

For such small differences in the concentration of the acetic acid as are involved in the determination of $\bar{v}$, the hydrogen-ion concentration given by (3) and the corresponding reaction velocity given by (2) are linear functions of x. It follows that the observed mean reaction velocity $\bar{v} = \Delta x/t$ should be very nearly identical with the actual velocity due to the catalytic action of the mixture $c\mathrm{HCl} + x\mathrm{CH_3{\cdot}CO_2H}$, where x is the mean concentration of the acetic acid for the interval t. Equation (2) may therefore be written in the form

$$k = \Delta x/[\mathrm{H}^+](e - \tfrac{1}{2}\Delta x)t \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the values of $[\mathrm{H}^+]$ derived from (3) by the introduction of $K = 1{\cdot}85 \times 10^{-5}$ are used to calculate k from (4), it is found that k diminishes slowly as the concentration of the acetic acid increases. This suggests that the ionisation constant of the acetic acid in the ester solution is less than the value for pure aqueous solutions. In view of the fact that the hydrogen-ion concentration of aqueous solutions of weak acids is very appreciably reduced on the addition of substances such as ethyl alcohol, acetone, etc., it may indeed be expected that ethyl acetate, as a substance of low dielectric capacity, will produce a similar and even greater effect. Evidence of this reduction is afforded by the data obtained in the experiments of Dawson and Lowson (*loc. cit.*) on the rate of ester hydrolysis with acetic acid as catalyst, from which the value derived for $k\sqrt{K}$ is $2{\cdot}61 \times 10^{-5}$. Combining this with $k = 6{\cdot}5 \times 10^{-3}$, we obtain $K = 1{\cdot}6 \times 10^{-5}$ for the ionisation constant of acetic acid in a 0·4-molar solution of ethyl acetate.

In qualitative agreement with this result, it has been found that the conductivity (κ) at 25° of a 0·1N-solution of acetic acid in the above solvent (40 c.c. of ester per litre) is only $4{\cdot}57 \times 10^{-4}$ mho as compared with $\kappa = 5{\cdot}30 \times 10^{-4}$ mho when the solvent is pure water. This difference may be due in part to a change in the ionic mobilities, but there can be little doubt that the presence of the ester reduces the ionisation of the acetic acid. In the presence of hydrochloric acid the reduction may be counteracted to some extent as a result of the increase in the ionic concentration in the environment of the dissociable acetic acid molecules, but since the hydrochloric acid concentrations concerned are very small, this effect is probably not of much importance. A detailed investigation of the relations in question might enable us to express the ionisation constant as a function of the concentrations of the ester and of the hydrochloric acid, but the necessary data are not available. In these circumstances the ionisation constant has tentatively been given the value $K = 1\cdot6 \times 10^{-5}$, in terms of which it is possible, as will be shown, to give a satisfactory account of the observed reaction velocities.

The results are summarised in Table II. Col. 1 gives the time intervals in minutes; Col. 2 the quantities of ester in mols. per litre hydrolysed during these intervals; Col. 3 the mean reaction velocities $\Delta x/t \,.\, 10^7$; Col. 4 the mean ester concentrations $(e - \Delta x/2)$; Col. 5 the mean acetic acid concentrations $(x \,.\, 10^3)$; Col. 6 the mean hydrogen-ion concentrations $[H^+] \,.\, 10^3$; and Col. 7 the velocity coefficients $(k \,.\, 10^3)$ derived from equation (4). It is apparent that

TABLE II.

t.	$\Delta x \,.\, 10^3$.	$\bar{v} \,.\, 10^7$.	$e - \frac{1}{2}\Delta x$.	$x \,.\, 10^3$.	$[H^+] \,.\, 10^3$.	$k \,.\, 10^3$.	
			0·0002*N*-HCl.				
1230	0·348	2·83	0·206	0·174	0·212	6·48	
1431	0·392	2·74	0·206	0·196	0·213	6·24	
2543	0·764	3·00	0·206	0·382	0·225	6·48	
3078	0·964	3·13	0·206	0·482	0·231	6·58	
4213	1·332	3·16	0·205	0·666	0·241	6·40	
6798	2·39	3·51	0·205	1·195	0·267	6·42	
			0·0005*N*-HCl.				
1523	1·05	6·89	0·206	0·525	0·516	6·49	
2802	1·96	7·00	0·205	0·980	0·529	6·45	
4170	3·01	7·22	0·205	1·50	0·543	6·49	
5711	4·22	7·39	0·204	2·11	0·559	6·48	
5864	4·33	7·38	0·204	2·16	0·560	6·46	
8576	6·54	7·63	0·203	3·27	0·587	6·40	
2905	2·52	8·63	0·205	6·26	0·650	6·51	*
5703	5·01	8·78	0·204	7·50	0·674	6·39	
2859	2·79	9·76	0·205	11·40	0·741	6·42	†
5709	5·70	9·98	0·203	12·85	0·763	6·45	
8572	8·62	10·06	0·202	14·3	0·785	6·34	
			0·001*N*-HCl.				
2725	3·71	13·62	0·204	1·85	1·027	6·50	
2987	4·08	13·66	0·204	2·04	1·030	6·51	
3970	5·46	13·75	0·203	2·73	1·040	6·51	
5744	8·06	14·03	0·202	4·03	1·059	6·56	
6988	9·84	14·07	0·201	4·92	1·072	6·52	
8630	12·20	14·12	0·200	6·10	1·088	6·50	
			0·002*N*-HCl.				
1422	3·81	26·8	0·204	1·90	2·015	6·52	
1560	4·16	26·7	0·204	2·08	2·015	6·47	

* In these experiments acetic acid was added at the commencement to give a 0·005*N*-solution.

† Initial addition of acetic acid to give a 0·01*N*-solution.

the measured reaction velocities can be satisfactorily interpreted in terms of equation (4), for the variations in the tabulated values of k are within the limits which are attributable to experimental error.

With reference to the magnitude of the autocatalytic effects which are involved, it may be noted that the observed velocity increases by about 25% in the experiments with 0·0002*N*-hydrochloric acid, and by about 40% in those with 0·0005*N*-hydrochloric acid. The maximum velocity ($\bar{v} = 10{\cdot}06 \times 10^{-7}$) in the latter series corresponds with a solution in which the mean concentration of the acetic acid is nearly thirty times as great as the concentration of the hydrochloric acid. These figures serve to indicate the range of the variations which are associated with the measurements recorded in the table.

The results afford additional support for the contention that the rate of hydrolysis of ethyl acetate is determined by the hydrogen-ion concentration of the solutions. Considered in the light of Brönsted's " intermediate complex " theory, they would seem to indicate that the primary stage of the reaction consists in the interaction of the hydrogen ion with the electrically neutral ethyl acetate molecule.

Summary.

The catalytic effects produced by hydrochloric acid in the hydrolysis of ethyl acetate have been examined over a wide range of acid concentrations.

A method for the elimination of autocatalytic effects and for the determination of initial velocities is described.

For concentrations of hydrochloric acid between 0·0002 and 0·2 mol. per litre, the initial velocity is proportional to the concentration of the acid.

At all stages the velocity is determined by the hydrogen-ion concentration of the solution.

The catalytic activity of the hydrogen ion would thus appear to be determined by its concentration and not by its thermodynamic activity.

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