

LVII.—*Acid and Salt Effects in Catalysed Reactions.*  
 Part XIX. *The Catalytic Activity of Chloroacetic Acid in the Hydrolysis of Ethyl Acetate.*

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PREVIOUS observations (J., 1927, 2444) on the rate of hydrolysis of ethyl acetate with acetic acid as catalyst indicate that catalytic activity must be ascribed to both the acetic acid molecule and the acetate ion. When the concentration of the acetic acid is fixed and gradually increasing quantities of sodium acetate are added, the reaction velocity passes through a minimum, and it has been shown that the connexion between the velocity and the logarithm of the hydrogen-ion concentration is closely represented by the so-called catalytic catenary. When chloroacetic acid is used as catalyst, the relations presented by the velocity measurements are much less simple, and the co-ordination of the effects has necessitated a more complete examination of the catalytic behaviour of the acid.

With reference to the general equation  $v = k_h[\text{H}^+] + k_a[\text{A}^-] + k_m[\text{HA}]$ , it may be pointed out in the first place that the coefficients  $k_a$  and  $k_m$  for acetic acid are very small compared with  $k_h$ . Since  $k_m$  increases and  $k_a$  diminishes with increase in the ionisation constant of the catalysing acid, it was anticipated that little difficulty would be experienced in obtaining evidence for the catalytic activity of the chloroacetic acid molecule. It was found, however, that the formation of hydrochloric acid by chlorine hydrolysis of the chloroacetate interferes with the direct determination of the rate of ester hydrolysis when the chloroacetate is present in any considerable quantity. The incidence of this reaction sets a limit to the reduction of the hydrogen-ion concentration of the chloroacetic acid solutions by the addition of the corresponding salt for the purpose of obtaining conditions under which the velocity of the reaction is no longer dominated by the catalytic effect of the hydrogen ion. Quite apart from the chlorine hydrolysis, such conditions are much more difficult to realise with chloroacetic than with acetic acid, for the increase in the  $k_m$  value in passing from acetic to chloroacetic acid is very much less than the corresponding increase in the ionisation constant.

In further illustration of the difficulties which are met with in the present series of experiments, a comparison may be made between the catalytic effects which are associated with chloroacetic acid in the hydrolysis of ethyl acetate and in the acetone-iodine reaction. For the latter, the value of  $k_m/k_h$  is about 35 times as large as it is for the former reaction. Whilst, therefore, the determination of  $k_m$  for chloroacetic acid as catalyst in the acetone reaction can be readily effected with considerable accuracy, it is apparent that the evaluation of  $k_m$  for the ester hydrolysis may be seriously interfered with by those indirect catalytic influences which have been discussed by Dawson and Key (J., 1928, 1239, 1248) under the name of inert-salt effects and by Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169) under the name of primary and secondary kinetic salt effects.

In the investigation of the catalytic effects produced by chloroacetic acid or by the corresponding acid-salt mixtures, it has, therefore, been necessary to take account of the chlorine hydrolysis of the catalyst and of the influence of ionic environment on the catalytic coefficients and on the ionisation constant of the acid. With regard to the chlorine hydrolysis, it may be shown that this is negligible in experiments with 0.05 and 0.1*N*-chloroacetic acid when the concentration of the added chloroacetate does not exceed 0.2 mol. per litre. At greater concentrations, the hydrochloric acid formed not only interferes with the direct determination of the quantity of ester which has been hydrolysed, but by interaction with the sodium chloroacetate it alters the ratio of chloroacetate to chloroacetic acid and therefore the hydrogen-ion concentration of the solution. If, however, the hydrolysis of the ester is confined to the early stages of the reaction, it may be shown that this alteration does not appreciably affect the measurement of the required reaction velocity.

In order to ascertain the influence of the variations in ionic environment, experiments have been made with solutions of sodium chloride, which has no direct catalytic action in the hydrolytic change. In the application of the results of these experiments, it is assumed that the changes produced by sodium chloride in  $k_h$  and  $K$  are the same as those which may be attributed to equivalent quantities of sodium chloroacetate. Some such assumption is inevitable, although there can be little doubt that the inert-salt effects are not generally independent of the nature of the constituent ions. The results previously obtained with potassium, sodium, and lithium chlorides in the study of the acetone-iodine reaction with acetic acid as catalyst (*loc. cit.*) show, indeed, very clearly that the inert-salt effect is not solely determined by the ionic strength of the solution but that specific influences are involved.

By restricting the reaction to its early stages, two other minor sources of disturbance have been avoided, namely, those associated with the catalytic action of the acetic acid formed and with the retarding effect of the reverse reaction.

The experiments were made at 25° with solutions which contained 20 c.c. (0.206*M*) of ethyl acetate per litre, and in the first instance attention will be directed to those observations which seem to establish the existence of a catalytic effect attributable to the molecule of chloroacetic acid. In these experiments, the catalytic influence of the hydrogen ion was reduced by the use of solutions which contained sodium chloroacetate and chloroacetic acid in the ratio 10 : 1. In order to eliminate the effect of chlorine hydrolysis, parallel experiments were made with solutions which contained no ester. The corresponding pairs of solutions were titrated after equal intervals of time and the difference in the titres obviously affords a measure of the rate at which the ester is hydrolysed. The results of two such experiments are shown in Table I. The first row gives the time in minutes, the second shows the volume of 0.1*N*-sodium hydroxide required to neutralise 25 c.c. of the ester-free solution, whilst the third gives the figures for the ethyl acetate solution. The fourth row represents the difference (*y*) which affords a measure of the ester hydrolysed, and the fifth gives the values ( $\times 10^4$ ) of the specific velocity  $v = 1/t \cdot \log_e a/(a - y)$  with  $a = 51.5$ .

TABLE I.

0.1 <i>N</i> -CH <sub>2</sub> Cl·CO <sub>2</sub> H + 1.0 <i>N</i> -CH <sub>2</sub> Cl·CO <sub>2</sub> Na.					
<i>t</i> (mins.) .....	4,100	9,900	15,500	21,260	28,470
C.c. alkali (no ester) .....	0.31	1.20	2.17	3.19	4.36
C.c. alkali (with ester) ...	0.93	2.62	4.41	6.20	8.40
<i>y</i> .....	0.62	1.42	2.24	3.01	4.04
<i>v</i> · 10 <sup>4</sup> .....	0.0295	0.0283	0.0287	0.0283	0.0287
				Mean	0.0285
0.05 <i>N</i> -CH <sub>2</sub> Cl·CO <sub>2</sub> H + 0.50 <i>N</i> -CH <sub>2</sub> Cl·CO <sub>2</sub> Na.					
<i>t</i> (mins.) .....	4,060	9,850	15,450	21,220	28,460
C.c. alkali (no ester) .....	0.08	0.30	0.49	0.75	1.01
C.c. alkali (with ester) ...	0.53	1.44	2.31	3.19	4.31
<i>y</i> .....	0.45	1.14	1.82	2.44	3.30
<i>v</i> · 10 <sup>4</sup> .....	0.0216	0.0227	0.0233	0.0229	0.0233
				Mean	0.023

From the above table it is apparent that the hydrolysis of the ester proceeds in accordance with the equation for a unimolecular change with a constant catalytic factor. The collective results obtained in the present series of experiments afford no evidence of a measurable catalytic effect which might be attributed to the chloroacetic anion. This accords with the fact that the catalytic activity of the anion of the much weaker acetic acid is already very

small (see Dawson and Lowson, *loc. cit.*). Since, moreover, the experimental results with acetic acid as catalyst leave no room for a measurable water effect, it follows that the mean value of the specific velocity  $v$  affords a measure of the sum of the effects due to the hydrogen ion ( $v_h$ ) and the chloroacetic acid molecule ( $v_m$ ), or

$$v = v_h + v_m = k_h[\text{H}^+] + k_m[\text{HA}] = (k_h - k_m)[\text{H}^+] + k_m c . \quad (1)$$

This equation may be used for the derivation of  $k_m$  provided that the value of  $k_h$  (Table II, col. 4) and the value of  $K$  (Table II, col. 6) from which  $[\text{H}^+]$  is derived by means of the equation  $[\text{H}^+] = k(c - [\text{H}^+])/[\text{A}^-]$  are those which correspond with the salt concentration of the solution under investigation. For the first experiment (1*N*-salt),  $k_h = 8.14 \times 10^{-3}$  and  $K = 2.40 \times 10^{-3}$  (compare Table II), whence  $k_m = 0.090 \times 10^{-4}$ . For the second experiment (0.5*N*-salt),  $k_h = 7.32 \times 10^{-3}$  and  $K = 2.53 \times 10^{-3}$ , whence  $k_m = 0.095 \times 10^{-4}$ .

The values of  $k_m$  derived in this way are in close agreement and would seem to show that the undissociated chloroacetic acid has a measurable catalytic effect. For our purpose the value of  $k_m$  may be taken as  $0.09 \times 10^{-4}$ , and in accordance with the evidence afforded by previous observations on the acetone-iodine reaction, which show that the catalytic activity of the acetic acid molecule and of the acetic anion varies but slightly with the salt concentration, it is probable that this value is not appreciably affected by the ionic environment.

*Dependence of  $k_h$  and  $K$  on the Reaction Medium.*—On the assumption that the variations in  $k_h$  and  $K$  are independent of the nature of the uni-univalent salt which is present in the solutions, these variations have been derived from reaction-velocity measurements in sodium chloride solutions. To obtain the required values of  $k_h$ , measurements were made with 0.01*N*-hydrochloric acid as catalyst, and the results are summarised thus :

NaCl (mols./litre)	0	0.05	0.2	0.5	1.0	2.0	3.0	4.0
$k_h \cdot 10^3$ .....	6.47	6.57	6.87	7.35	8.09	9.85	11.80	14.10

These values of  $k_h$  are in close agreement with those given by Harned and Hawkins (*J. Amer. Chem. Soc.*, 1928, 50, 85) from experiments with 0.1*N*-hydrochloric acid as catalyst. The relation between  $k_h$  and the salt concentration is represented by a straight line if the latter is not much greater than 2 mols. per litre, but in more concentrated solutions the velocity increases somewhat more rapidly. Similar relations have already been noted in corresponding experiments with the acetone-iodine reaction.

The variations in  $K$  have been derived by combining the hydrochloric acid experiments with a corresponding series in which

0.1*N*-chloroacetic acid was used as catalyst. In Table II, col. 1 gives the concentration of the sodium chloride, col. 3 the specific reaction velocity  $v = 1/t \cdot \log_e a/(a - y)$ , col. 4 the value of  $k_h$  given by the smooth curve which represents the results obtained with hydrochloric acid, col. 5 the hydrogen-ion concentration derived from  $[H^+] = (v - k_m c)/(k_h - k_m)$  (compare equation 1), and col. 6 the ionisation constant  $K = [H^+]^2/(c - [H^+])$ . In addition the ionic strengths of the various solutions are shown in col. 2. Since the ionisation constant varies rapidly with the salt concentration in dilute solutions, particular attention has been given to the influence of small quantities of sodium chloride.

TABLE II.  
0.1*N*-CH<sub>2</sub>Cl·CO<sub>2</sub>H + *x*NaCl.

<i>x</i> .	$\mu$ .	$v \cdot 10^4$ .	$k_h \cdot 10^3$ .	[H <sup>+</sup> ].	$K \cdot 10^3$ .
0	0.012	0.775	6.50	0.0118	1.58
0.01	0.022	0.799	6.52	0.01215	1.68
0.02	0.032	0.816	6.53	0.0124	1.75
0.03	0.042	0.836	6.55	0.01265	1.83
0.04	0.052	0.845	6.57	0.01275	1.86
0.05	0.063	0.875	6.58	0.0132	2.01
0.10	0.11	0.918	6.66	0.01365	2.16
0.20	0.21	0.970	6.82	0.0141	2.31
0.30	0.31	1.005	6.98	0.0143	2.39
0.50	0.51	1.085	7.32	0.0147	2.53
1.0	1.01	1.177	8.14	0.01435	2.40
2.0	2.01	1.304	9.90	0.0131	1.98
3.0	3.01	1.370	11.80	0.01155	1.51
4.0	4.01	1.330	14.10	0.00938	0.97

The concentration of the ester in the above experiments was for the most part 20 c.c. per litre, but on account of "salting out" this was reduced to 8.0 c.c. per litre in the case of the 3 and 4*M*-salt solutions. That this reduction in the ester concentration does not affect the comparability of the results is shown by the fact that the observed velocity for the 2*M*-salt solution is very nearly the same for the two ester concentrations.

The variation of  $K$  with the salt concentration is similar to that shown by corresponding data for the acetone-iodine reaction. In so far as the dilute salt solutions are concerned, the two series of data are not, however, strictly comparable, for the acetone experiments were made with solutions which contained a small quantity of potassium iodide.

With regard to the accuracy of the  $K$  values, it should be noted that the hydrogen-ion concentrations from which these are derived depend on measurements of the reaction velocity with both hydrochloric and chloroacetic acids. If the possible error in the observed velocity is assumed to be 1%, it is evident that the error in the individual values of  $K$  may be as high as 4%. The values derived

from  $K$ - $x$  graphs are probably more accurate than this, and such smoothed values are actually used in applying these preliminary observations to the interpretation of the experiments which are to be described.

Since the ionic strength of the sodium chloride-free solution is 0.012, it may be anticipated that the value of  $K$  for a solution in which the ionic effects are negligible will be appreciably less than the first recorded value, *viz.*,  $1.58 \times 10^{-3}$ . In this connexion, attention may be directed to the method described by Dawson, Hall, and Key (J., 1928, 2844) for the determination of the limiting value of  $K$  for reaction velocity data. This method when applied to the data for chloroacetic acid and the acetone-iodine reaction gave for the limiting value  $K_0 = 1.51 \times 10^{-3}$ . By its application to the data for the hydrolysis of ethyl acetate, we obtain  $K_0 = 1.48 \times 10^{-3}$ . These results suggest that the value of the ionisation constant of chloroacetic acid in very dilute solution may be taken as  $K_0 = 1.5 \times 10^{-3}$ .

*Catalytic Activity of Chloroacetic Acid in Presence of Chloroacetate.*—Experiments with acid-salt mixtures of the series  $c\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + x\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$  ( $c$  constant,  $x$  variable) show that the reaction velocity falls continuously as the concentration of the chloroacetate increases. On account of chlorine hydrolysis, the investigation of such mixtures cannot, however, be extended to solutions for which  $x$  is much greater than unity.

The results for two series of constant-acid mixtures are recorded in Table III. The first line of figures gives  $x$ ; the second and third the corresponding values of  $k_h$  and  $K$ ; the fourth shows the observed velocities given by  $v = 1/t \cdot \log_e a/(a - y)$ , and the fifth the velocities calculated from equation (1).

TABLE III.

0.1N- $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + x\text{N}\cdot\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ .

$x$ .....	0	0.02	0.05	0.1	0.2	1.0
$k_h \cdot 10^3$ .....	6.50	6.53	6.58	6.66	6.82	8.14
$K \cdot 10^3$ .....	1.60	1.80	2.00	2.15	2.35	2.40
$v \cdot 10^4$ obs. ....	0.775	0.413	0.234	0.142	0.086	0.0285
$v \cdot 10^4$ calc. ....	0.780	0.426	0.245	0.146	0.088	0.0285

0.05N- $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + x\text{N}\cdot\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ .

$x$ .....	0	0.02	0.05	0.1	0.2	0.5
$k_h \cdot 10^3$ .....	6.50	6.53	6.58	6.66	6.82	7.32
$K \cdot 10^3$ .....	1.55	1.80	2.00	2.15	2.35	2.50
$v \cdot 10^4$ obs. ....	0.523	0.224	0.122	0.071	0.041	0.023
$v \cdot 10^4$ calc. ....	0.527	0.236	0.126	0.073	0.044	0.023

From the general agreement between the observed and the calculated velocity it may be inferred that the specific rate of hydrolysis

of the ester is determined by the sum of the catalytic effects which are due to the hydrogen ion and the chloroacetic acid molecule. If the variations of  $k_h$  and  $K$  with the ionic concentration are not taken into account, the differences between the observed and calculated velocities are very large, as may be seen when the latter are derived from the limiting values  $k_h = 6.50 \times 10^{-3}$  and  $K = 1.5 \times 10^{-3}$ . For the successive experiments with 0.1*N*-chloroacetic acid in Table III these calculated velocities are 0.756, 0.368, 0.188, 0.102, 0.056, and 0.018.

In further support of the interpretation given to the experiments of Table III, measurements have also been made with solutions of chloroacetic acid-chloroacetate mixtures in which the total salt concentration was kept constant at 1 mol. per litre by the addition of sodium chloride. In these circumstances the inert-salt factor remains unchanged and the observed reaction velocities can be satisfactorily expressed in terms of equation (1) with constant values of  $k_h = 8.14 \times 10^{-3}$  and  $K = 2.40 \times 10^{-3}$  (compare Table II), as may be seen from Table IV.

TABLE IV.



$x$ .....	0	0.02	0.05	0.1	0.2	1.0
$v \cdot 10^4$ obs. ....	1.177	0.656	0.353	0.195	0.104	0.0285
$v \cdot 10^4$ calc. ....	1.175	0.653	0.354	0.195	0.105	0.0285

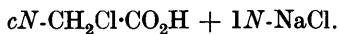
*Influence of Concentration on the Catalytic Activity of Free Chloroacetic Acid.*—Variations in the catalysing power of an acid with its concentration were first used by Dawson and Powis (J., 1913, **103**, 2135) for the determination of the coefficients which express the catalytic activity of undissociated acid molecules. The numbers derived in this way for the acetone-iodine reaction have since been confirmed by experiments with acid-salt mixtures. It should be clearly recognised, however, that the successful application of the method depends on the magnitude of the ratio  $k_m/k_h$ . The measured velocity represents the sum of the partial velocities due to the ionised and to the un-ionised acid, and since the ionic strength of the solution, and therefore the ionisation constant of the acid, increases with the total concentration of the acid, it follows that the increase in the catalytic effect due to the ionised acid will be greater than it would have been if the ionisation constant of the acid were independent of its concentration. If  $k_m/k_h$  is relatively large, this variation of  $K$  may not interfere very much with the determination of  $k_m$ , but will obviously do so if  $k_m/k_h$  is very small. For this reason, the variation of the velocity of hydrolysis of ethyl acetate with the concentration of the catalysing acid cannot be used for the determination of  $k_m$  for

chloroacetic acid, although this method is readily applicable in the case of the acetone-iodine reaction. Furthermore, there is reason to believe that the changes in  $K$  due to ionic environment cannot be assumed to remain the same when a univalent metal ion is replaced by the stoichiometrically equivalent quantity of "hydrogen" ion. In these circumstances it is not possible to calculate the velocities for the chloroacetic acid at different concentrations with the requisite degree of accuracy. On the other hand, the observed velocities may be utilised for the derivation of  $K$  values by the application of equation (1). The results obtained with  $k_h = 6.50 \times 10^{-3}$  and  $k_m = 0.09 \times 10^{-4}$  are as follows :

$c$ .....	0.01	0.02	0.05	0.1	0.2
$v \cdot 10^4$ obs. ....	0.209	0.312	0.523	0.775	1.140
$K \cdot 10^3$ .....	1.51	1.50	1.52	1.58	1.64

The anticipated increase in the ionisation constant is thus actually found, but the increase is small and too much significance cannot be attached to the individual values. The difficulties associated with the auto-ionising influence which has been referred to may, however, be obviated by using a moderately concentrated salt solution as solvent instead of water. Under these conditions the ionisation constant of the acid should be independent of its concentration if this is not made too large. The experimental results for a series of chloroacetic acid solutions with 1*N*-sodium chloride as solvent are summarised below. The calculated reaction velocities are those derived from equation (1), with  $k_h = 8.14 \times 10^{-3}$ ,  $K = 2.40 \times 10^{-3}$ , and  $k_m = 0.09 \times 10^{-4}$ .

TABLE V.



$c$ .....	0.005	0.01	0.02	0.05	0.1	0.2	0.3
$v \cdot 10^4$ obs. ....	0.202	0.314	0.470	0.804	1.177	1.70	2.09
$v \cdot 10^4$ calc. ....	0.201	0.314	0.476	0.803	1.175	1.70	2.11

The differences between the observed and calculated velocities in this series are well within the probable errors of experiment, and it would therefore seem that the catalytic activity of chloroacetic acid can be represented in terms of equation (1) with a constant value of the ionisation constant when the nature of the solvent is such that the ionic environment is sensibly constant.

#### Summary.

The foregoing series of experiments shows that the catalytic effects produced by chloroacetic acid in the hydrolysis of ethyl acetate can be expressed by  $v = k_h[\text{H}^+] + k_m[\text{HA}]$ , provided that the variation of  $k_h$  and  $K$  with the ionic environment is taken into account. The effect of the chloroacetate ion appears to be very small. In sodium



chloride solutions of gradually increasing concentration, the value of  $k_h$  shows a continuous increase, whilst  $K$  passes through a maximum at about  $0.5M$ -concentration.

When constancy of ionic environment is provided for, the catalytic effects produced by free chloroacetic acid and by mixtures of this with chloroacetate can be satisfactorily explained in terms of fixed values of the ionisation constant and of the catalytic coefficients. The ratio  $k_m/k_h$  for chloroacetic acid in the hydrolysis of ethyl acetate is about  $1/700$ , compared with  $1/20$  for the catalysing action of the acid in the acetone-iodine reaction.

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