CCCCXXVII.—*Acid and Salt Effects in Catalysed Reactions. Part XVIII. The Dynamics of Autocatalysed Ester Hydrolysis.*

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Recent experiments by the authors (this vol., p. 2146) have shown that the initial speed of the hydrolysis of ethyl acetate with hydrochloric acid as catalyst is proportional to the concentration of the acid when this is varied between 0·0002 and 0·2 mol. per litre. If the concentration of the hydrochloric acid is less than 0·01 mol. per litre, the course of the reaction is modified by the catalytic action due to the acetic acid produced. The relative importance of this autocatalytic effect increases as the concentration of the hydrochloric acid diminishes, and it is not possible in practice to determine the initial velocity of the reaction when this concentration falls below 0·0002 mol. per litre.

The present experiments are, for the most part, concerned with the course of the reaction when foreign catalysts are absent, *i.e.*, when the only catalytic effects involved are those which are attributable, directly or indirectly, to the solvent or to the acetic acid which is set free in the reaction. In this connexion, reference should be made to the experiments of Wijs (*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514) on the autohydrolysis of methyl acetate, in which the progress of the reaction was followed by measurements of the electrical conductivity of the solution, and it was shown that the reaction velocity passed through a minimum value. The observations were, however, confined to a very small period in the early stages of the reaction, but this was sufficient for the main object of the experiments, which was to obtain a value for the ionisation constant of water.

In its entirety, the autocatalytic hydrolysis of an ester such as ethyl acetate represents a complex process in which the reaction velocity passes through a minimum and a maximum value. The attainment of maximum velocity is not in any way connected with the reversibility of the reaction, although this alone would of course suffice to determine the incidence of a maximum. If, however, the reverse reaction has to be taken into account, the mathematical treatment of the problem becomes extremely complex, and for this reason the investigation has been confined to that phase of the complete reaction for which the influence of the oppositely directed esterification process can be neglected. Within these limits, and in accordance with current views relating to catalytic effects, the general equation for the reaction velocity may be written

$$dx/dt = \{k_h[\mathrm{H^+}] + k_{\mathrm{OH}}[\mathrm{OH^-}] + k_w[\mathrm{H_2O}] + k_a[\mathrm{Ac^-}] + k_m[\mathrm{HAc}]\}\,(a - x)[\mathrm{H_2O}] \quad . \quad . \quad (1)$$

in which the catalytic coefficients are represented by the usual symbols and $(a - x)$ is the concentration of the ester after time t. Since the concentrations of the several catalytic entities are connected by $[\mathrm{H^+}]\,.\,[\mathrm{OH^-}] = K_w$, $[\mathrm{Ac^-}] = [\mathrm{H^+}] - [\mathrm{OH^-}]$, and $[\mathrm{HAc}] = x - [\mathrm{Ac^-}]$, equation (1) may be written

$$dx/dt = \{(k_h - k_m + k_a)[\mathrm{H^+}] + (k_{\mathrm{OH}} + k_m - k_a)K_w/[\mathrm{H^+}] + k_m x + k_w[\mathrm{H_2O}]\}\,(a - x)[\mathrm{H_2O}]$$

and from a consideration of the relative values of $k'_h = 6{\cdot}5 \times 10^{-3}$, $k'_{OH} = 6{\cdot}5$, $k'_m = 1{\cdot}5 \times 10^{-6}$, $k'_a = 2 \times 10^{-7}$, and k'_w, which is too small to have a measurable value assigned to it, it may be readily shown that the equation may be further reduced to the form

$$dx/dt = \{k'_h[H^+] + k'_{OH}K_w/[H^+]\}\,(a - x) \quad . \quad . \quad (2)$$

where $k'_h = k_h[H_2O]$ and $k'_{OH} = k_{OH}[H_2O]$.

In terms of this equation it is convenient to distinguish two successive stages of the autocatalysed reaction. In the first stage the catalytic effect corresponds with the joint action of the hydrogen and the hydroxyl ion, and the concentration of the ester is practically constant. In the second stage the catalytic action is confined to the hydrogen ion, and the concentration of the ester gradually diminishes. There is, of course, no breach of continuity in passing from the first to the second stage, but it is convenient, although more or less arbitrary, to select as the end of the first stage that point at which the catalytic effect of the hydroxyl ion has fallen to 1% of the catalytic effect due to the hydrogen ion.

Before proceeding to the further examination of equation (2), reference may be made to the nature of the experimental observations. The solution of the ester (40 c.c. per litre = $0{\cdot}412M$) was prepared by dissolving carefully purified ethyl acetate in conductivity water, the temperature being kept at 25·0°. The acetic acid formed was determined after suitable time intervals by titration. In the early stages of the reaction, 25 c.c. samples were titrated with $0{\cdot}01N$-alkali, and in the later stages, 10 c.c. samples with $0{\cdot}1N$-alkali.

The earlier experiments showed wide differences in the results obtained; for instance, the time required for the production of acetic acid in $0{\cdot}0002M$ concentration varied from about 3000 to 10,000 minutes. Investigation of the cause of these discrepancies showed that the slower speeds of the reaction were mainly, if not entirely, due to the retarding effect of alkali from the walls of the glass containing vessel. The later experiments were therefore carried out in fused silica vessels, and it was thus possible to obtain reproducible results without difficulty. In order to acquire information relative to the influence of small quantities of alkali, parallel experiments in silica flasks were made with ester solutions to which various small quantities of sodium hydroxide were added. It may be readily shown that the hydroxide is rapidly converted into acetate, and that the course of the reaction as represented by the x–t curve is sensibly the same as if the equivalent amount of sodium acetate had been added at the outset.

In the actual application of equation (2), it has been found convenient to express the hydrogen-ion concentration of the acid solution in terms of the ionisation constant of the acid. If $[H^+] = rK$, then $[HA] = r^2K$, and the total concentration of the acid is $r(r + 1)K$. This quantity r may be termed the ionisation ratio, the relation of which to the degree of ionisation is given by $r = (1 - \alpha)/\alpha$ or $\alpha = 1/(r + 1)$. In terms of r, the expression for the ionisation constant takes the form $K = c/r(r + 1)$, where c is the total acid concentration.

First Stage of the Autocatalysed Reaction.—The quantity of acetic acid formed at the end of the first stage is far too small to be determined titrimetrically and our concern with this stage is therefore limited to the estimation of the period of time which it occupies. The equation for the reaction velocity is

$$dx/dt = \{k'_h[H^+] + k'_{OH}K_w/[H^+]\}\ a \quad . \quad . \quad . \quad (3)$$

and when the acid produced by the reaction is fully ionised, or $[H^+] = x$, this can be integrated quite simply (compare Dawson, J., 1927, 458). This, however, is no longer the case when the acid formed is weak and its hydrogen-ion concentration is given by $[H^+] = \sqrt{(K/2)^2 + Kx} - K/2$; in these circumstances the procedure followed in the calculation of the required time involves considerations which are associated with the catenary form of the v–log $[H^+]$ curve. The method employed is general in the sense that it may be applied in the case of all autocatalysed reactions of similar type.

The hydrogen-ion concentration at which the reaction velocity passes through its minimum value is given by $[H^+]_i = \sqrt{k'_{OH} \cdot K_w/k'_h}$, and if K_w is taken as 10^{-14}, we obtain $[H^+]_i = 0{\cdot}32 \times 10^{-5}$, or since the value of K for acetic acid in $0{\cdot}4M$-ethyl acetate solution is $1{\cdot}6 \times 10^{-5}$, $[H^+]_i = 0{\cdot}2K$, or $r_i = 0{\cdot}2$.

If the hydrogen-ion concentration is expressed in terms of $[H^+]_i$ such that $[H^+]/[H^+]_i = n$, then equation (3) may be written as

$$dx/dt = k'_h[H^+]_i(n + 1/n)a \quad . \quad . \quad . \quad . \quad (4)$$

according to which 99% of the total catalytic effect is due to the hydrogen ion when $n = 10$, *i.e.*, when $[H^+] = 2K$. The value $r = 2$, which corresponds with $x = 6K$, may thus be identified with the end of the first stage of the reaction. For the calculation of the time required to reach this point, the complete stage may be divided into a series of small intervals, Δt, for each of which $\Delta x = \Delta\overline{r(r + 1)}K = K\Delta q$, where q measures the concentration of the acid in terms of K. If, now, $\bar{v}$ is the mean velocity for the interval characterised by the mean reduced hydrogen-ion concentration $\bar{n}$, then according to equation (4) we have

$$\Delta t = \Delta x/\bar{v} = K\Delta q/[k'_h[\mathrm{H}^+]_i(\bar{n} + 1/\bar{n})a]$$

Substituting $a = 0{\cdot}412$, $k'_h = 6{\cdot}5 \times 10^{-3}$, and $[\mathrm{H}^+]_i = 0{\cdot}2K$, we have

$$\Delta t = 1870\Delta q/(n + 1/\bar{n}),$$

whence the time required for the first stage is given by

$$t_1 = 1870\Sigma_{q=0}^{q=6}\Delta q/(\bar{n} + 1/\bar{n}) \quad . \quad . \quad . \quad . \quad (5)$$

in which $\bar{n} = \bar{r}/r_i$ where $\bar{r}$ is the mean value of r for the interval for which the mean reduced hydrogen-ion concentration is $\bar{n}$. The smaller the values of Δt and Δq, the greater will be the accuracy of t_1 given by equation (5). For the present purpose it is, however, sufficient to divide the first stage of the reaction into ten intervals, each of which corresponds with $\Delta r = 0{\cdot}2$. In this case the end of the first interval coincides with the point of minimum velocity. To illustrate the exact procedure and the nature of the results, the detailed figures are recorded in Table I. The first column gives the initial and final values of r for each interval; the second, the value of $\bar{n} = \bar{r}/r_i$; the third, that of $(\bar{n} + 1/\bar{n})$; the fourth, the initial and final values of q; the fifth, the value of Δq; and the sixth, that of Δt (in mins.).

TABLE I.

Autocatalysis : First Stage.

r'—r''.	$\bar{n}$.	$\bar{n} + 1/\bar{n}$.	q'—q''.	Δq.	Δt.
0·0—0·2	0·5	2·50	0·00—0·24	0·24	180
0·2—0·4	1·5	2·17	0·24—0·56	0·32	276
0·4—0·6	2·5	2·90	0·56—0·96	0·40	258
0·6—0·8	3·5	3·79	0·96—1·44	0·48	237
0·8—1·0	4·5	4·72	1·44—2·00	0·56	222
1·0—1·2	5·5	5·68	2·00—2·64	0·64	211
1·2—1·4	6·5	6·65	2·64—3·36	0·72	202
1·4—1·6	7·5	7·63	3·36—4·16	0·80	196
1·6—1·8	8·5	8·62	4·16—5·04	0·88	191
1·8—2·0	9·5	9·61	5·04—6·00	0·96	187

According to the table, the time required for the completion of the first stage of the reaction is $\Sigma\Delta t = 2160$ minutes. It may further be noted that the value of Δt for equal successive changes in the hydrogen-ion concentration diminishes regularly from the *M.V.* point onwards, *i.e.*, after the first interval. For the i^{th} interval, $\Delta q = 0{\cdot}16 + 0{\cdot}08i$, and since $\bar{n}$ approximates to i as the latter increases, it follows that Δt approaches a limiting value of $1870 \times 0{\cdot}08 = 149{\cdot}6$ minutes.

When the solution of the ester contains a small quantity of sodium acetate, the hydrogen-ion concentration corresponding with a given concentration of acetic acid (x) is reduced. If the concentration of the acetate (S mols. per litre) is expressed in terms of K, such that $S = mK$, then from $[\mathrm{HA}] = x - [\mathrm{H}^+] = [\mathrm{H}^+](S + [\mathrm{H}^+])/K$, we obtain $x = r(r + 1 + m)K$, or $q = r(r + 1 + m)$. Since the end of the first stage is reached when $r = 2$, it follows that the concentration of the acetic acid in the solution at this point increases with the quantity of sodium acetate present. The relation between the velocity of the autocatalysed reaction and the hydrogen-ion concentration is not, however, affected thereby, and the presence of sodium acetate makes no difference to the method described above for the calculation of the time which is occupied by the first stage of the autocatalysis. The values of q and t_1 for the quantities ($m = S/K$) of sodium acetate actually used in the experiments to be described are as follows :

m =	0	1·2	3·0	6·0
q =	6·0	8·4	12·0	18·0
t_1 =	2160	3215	4800	7450 mins.

Second Stage of the Autocatalysed Reaction.—The beginning of this stage is characterised by the circumstance that the hydroxyl ion ceases to play any sensible part in the hydrolysis. The equation for the reaction velocity may therefore be written

$$dx/dt = k'_h[\mathrm{H}^+](a - x) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

As in the case of the first stage, the form of the expression which gives the connexion between x and t is the same whether the hydrolysis takes place in pure water or in a solution which contains a small amount of alkali (sodium acetate). In these circumstances, it seems preferable to consider the general case in which the solution contains S mols. of acetate per litre. Since the hydrogen-ion concentration is given by $[\mathrm{H}^+] = \sqrt{(K + S)^2/4 + Kx} - (K + S)/2$, the previous equation may be put in the form

$$dx/dt = k'_h(a - x)(\sqrt{b^2 + Kx} - b) \quad . \quad . \quad (6a)$$

where $b = (K + S)/2$. Replacing $\sqrt{b^2 + Kx}$ by y, equation ($6a$) may be written

$$k'_h . dt = 2y \,.\, dy/(Ka + b^2 - y^2)(y - b),$$

which, on integration by the method of partial fractions, gives

$$k'_h t = \frac{2b}{Ka}\log(y - b) - \frac{1}{\sqrt{Ka + b^2} - b}\log(\sqrt{Ka + b^2} - y) + \frac{1}{\sqrt{Ka + b^2} + b}\log(\sqrt{Ka + b^2} + y) + \text{const.}$$

Replacing y by its equivalent in terms of x, then for initial and final values of x and t represented respectively by x', t', and x'', t'', this becomes

$$t'' - t' = \frac{1}{k'_h}\left\{\frac{2b}{Ka}\log\frac{\sqrt{b^2+Kx''}-b}{\sqrt{b^2+Kx'}-b} + \frac{1}{\sqrt{b^2+Ka}-b}\log\frac{\sqrt{b^2+Ka}-\sqrt{b^2+Kx'}}{\sqrt{b^2+Ka}-\sqrt{b^2+Kx''}} + \frac{1}{\sqrt{b^2+Ka}+b}\log\frac{\sqrt{b^2+Ka}+\sqrt{b^2+Kx''}}{\sqrt{b^2+Ka}+\sqrt{b^2+Kx'}}\right\} \quad . \quad . \quad . \quad . \quad (7)$$

In accordance with this equation, t'' may be used to denote the time required for the reaction to proceed from the end of the first stage ($[H^+] = 2K$) to any point in the second stage. For the later phases of the second stage in the absence of sodium acetate, the above equation reduces to the form

$$t'' - t' = \frac{1}{k'_h\sqrt{Ka}}\left\{\log\frac{\sqrt{a}+\sqrt{x''}}{\sqrt{a}+\sqrt{x'}} - \log\frac{\sqrt{a}-\sqrt{x''}}{\sqrt{a}-\sqrt{x'}}\right\} \quad (8)$$

which is identical with the equation previously derived (Dawson and Lowson, J., 1927, 2107) for the hydrolysis of ethyl acetate with acetic acid ($0{\cdot}1N$) as catalyst. Equation (8) follows, in fact, directly from equation (6) when the concentration of the acetic acid is large enough to permit of the substitution of $\sqrt{Kx}$ for $[H^+]$. In these circumstances,

$$v = k'_h\sqrt{Kx}\,(a - x)$$

whence

$$dv/dx = k'_h\sqrt{K}(a/2\sqrt{x} - 3\sqrt{x}/2) \quad . \quad . \quad . \quad (9)$$

according to which the reaction velocity passes through a maximum when $x = a/3$. Under the conditions of our experiments this maximum is reached before the reverse reaction begins to have any appreciable influence on the course of the hydrolysis.

EXPERIMENTAL.

With one exception the glass vessels used in our earlier experiments were found to retard the autocatalytic hydrolysis as compared with the reaction in silica vessels. In the exceptional case, the results were practically the same as for the silica flasks. Our experience in this connexion would suggest that the determination of the amount of acid produced by autohydrolysis of an ester in a given time might be made the basis of a practical method for the comparison of the " alkalinities " of samples of glass.

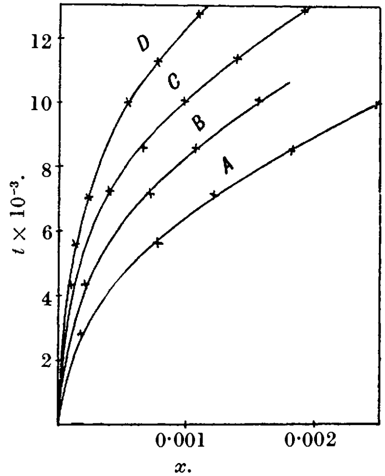
Table II gives the results for the early stages of autohydrolysis in silica flasks with and without the addition of alkali. For each experiment the first column of figures shows the number of c.c. of $0{\cdot}01N$-sodium hydroxide required for the titration of 25 c.c. of the ester solution; the second gives the acetic acid concentrations in mols. per litre, and the third the corresponding time intervals (minutes × 10^{-3}). The calculated times in the fourth column represent the sum of t_1 and t_2, where t_1 is the time occupied by the first stage and t_2 that required by the second stage; these numbers were derived from the theoretical x–t curves.

TABLE II.

Titre.	$x \cdot 10^3$.	$t \cdot 10^{-3}$ (obs.).	$t \cdot 10^{-3}$ (calc.).
	A. NaAc = nil.		
0·45	0·18	2·80	2·95
1·95	0·78	5·60	6·05
3·05	1·22	7·12	7·35
4·57	1·83	8·48	8·90
6·25	2·50	10·00	10·40
	D. NaAc = 96 × $10^{-6}N$.		
0·32	0·13	5·58	5·0
0·60	0·24	7·02	6·9
1·35	0·54	9·99	9·75
1·95	0·78	11·3	11·2
2·75	1·10	12·7	12·7
	B. NaAc = 19 × $10^{-6}N$.		
0·50	0·20	4·29	3·85
1·80	0·72	7·16	6·80
2·70	1·08	8·57	8·10
3·90	1·56	10·00	9·40
	C. NaAc = 48 × $10^{-6}N$.		
0·25	0·10	4·3	3·5
1·00	0·40	7·20	6·7
1·65	0·66	8·55	8·1
2·48	0·99	10·00	9·5
3·48	1·39	11·4	10·9
4·80	1·92	12·9	12·6

In comparing the calculated and observed times in the above table it should be recognised that the probable accuracy of the recorded acetic acid concentrations increases as the reaction proceeds, and that the error attaching to the first recorded values may be considerable. It appears that the observed rate of hydrolysis is somewhat more rapid than the theoretical in experiment A, and rather less rapid in B and C, whilst the agreement is very close in experiment D. The fact that the time-differences in A, B, and C are nearly independent of the amount of acetic acid formed suggests that the deviations are associated with the first stage of the autohydrolysis, and it seems probable that they are to be attributed to variations in the purity of the samples of conductivity water used in the several experiments. The experimental x–t curves are shown in Fig. 1.

FIG. 1.



Curves showing the rate of formation of acetic acid by autohydrolysis of ethyl acetate; (A) *in pure water;* (B), (C), *and* (D) *in presence of* 0·000019, 0·000048, *and* 0·000096 *mol. of sodium acetate per litre, respectively.*

Table III gives the results for an extended autocatalytic experiment in which the hydrolysis was allowed to proceed until the influence of the reverse reaction could no longer be ignored. Col. 1 shows the concentration (x) of the acetic acid formed (mols./litre), col. 2 the corresponding observed time interval (minutes $\times 10^{-3}$), and col. 3 the calculated time $t = t_1 + t_2$ derived by the method already explained.

TABLE III.

$x \cdot 10^2$.	$t \cdot 10^{-3}$, obs.	$t \cdot 10^{-3}$, calc.	$x \cdot 10^2$.	$t \cdot 10^{-3}$, obs.	$t \cdot 10^{-3}$, calc.
0·25	10·0	10·4	8·74	61·8	61·5
0·42	12·8	14·0	10·19	67·5	67·2
1·04	20·0	20·6	12·06	75·1	74·5
1·88	27·2	27·5	13·86	81·9	81·5
2·75	33·0	33·0	16·05	90·6	89·8
3·97	40·2	39·5	17·8	97·6	96·5
5·36	47·4	47·2	19·6	105·0	103·5
6·51	53·1	52·5	21·37	112·5	110·5
7·72	60·7	59·8	22·6	117·9	116·0

The above experiment was continued until about 50% of the original ester had been hydrolysed, at which point the velocity of the reverse reaction is about 1/70th of that of the hydrolytic process. This point may thus be taken to represent approximately the end-point of the reaction in so far as the validity of the equation derived for the second stage in the autohydrolysis is concerned. The tabulated numbers show that the observed progress of the reaction is in close agreement with the combined requirements of equations (5) and (7). It may be inferred that the course of the reaction can be interpreted in terms of the catalytic action of the hydrogen and hydroxyl ions, and that the speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to be measured.

With reference to the variations in velocity during the autohydrolysis, it may be noted that the maximum velocity given by $v_{\text{max.}} = k'_h\sqrt{Kx}(a - x)$ with $x = a/3$ is $2{\cdot}64 \times 10^{-6}$ mol. per litre per minute, and the minimum velocity given by $v_{\text{min.}} = 2a\sqrt{k'_h k'_{\text{OH}} K_w}$ is $1{\cdot}69 \times 10^{-8}$ mol. per litre per minute. The ratio of these velocities is thus proportional to the square root of the ester concentration, and for the concentration used in our experiments is equal to 156.

Summary.

The autocatalysed hydrolysis of ethyl acetate, in so far as this is not appreciably affected by the reverse reaction, has been studied by experiments in fused silica vessels.

The reaction may be divided into two stages, in the first of which the velocity is determined by the joint catalytic action of the

hydrogen and hydroxyl ions, and in the second by the catalytic activity of the hydrogen ion.

Equations are derived from which the time required to reach any given point may be calculated.

The retarding influence of small amounts of alkali is shown to be in accord with theoretical requirements.

It would seem that the speed of the uncatalysed reaction and the catalytic activity of the water molecules are too small to have any measurable influence on the course of the reaction.

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