

CCLXXIX.—*Acid and Salt Effects in Catalysed Reactions. Part X. The Hydrolysis of Ethyl Acetate with Acetic Acid as Catalyst.*

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IN presence of a strong acid, the rate of hydrolysis of ethyl acetate in dilute aqueous solution is determined by the difference between two reaction velocities which are proportional, respectively, to the concentration of the unhydrolysed ester and to the square of the concentration of the hydrolysed ester.

The integration of the differential equation, which takes account of the two opposed reactions, leads to a formula of very complicated type (compare Harned and Pfanstiel, *J. Amer. Chem. Soc.*, 1922, 44, 2193), and on this account it is customary to consider the reaction as non-reversible and to replace the total initial concentration of the ester by that corresponding with the ester which has been hydrolysed when the state of equilibrium is reached.

Since the experiments to be described by us are concerned, *inter alia*, with the determination of an accurate value for the catalytic coefficient of the hydrogen ion, it has seemed necessary to inquire to what extent and under what conditions the neglect of the reverse reaction affords a constant which may be taken as a measure of the true hydrolytic coefficient k_r in the equation for the reversible change. The latter may be written

$$dx/dt = k_r(w - x)(a - x) - k'_r x^2,$$

in which w represents the molar concentration of water and a that of the total ester in the original solution.

Since under the conditions of the experiments to be described x may be neglected in comparison with w , and k'_r may be replaced

by $K_e k_r$, where K_e is the equilibrium constant, the above equation assumes the form

$$dx/dt = k_r\{w(a - x) - K_e x^2\} \quad . \quad . \quad . \quad (1)$$

The two simplified equations which have been compared with this are

$$dx/dt = k_0 w(a - x) \quad . \quad . \quad . \quad . \quad (2)$$

and

$$dx/dt = k_e w(a_e - x) \quad . \quad . \quad . \quad . \quad (3)$$

in which k_0 refers to the velocity expressed in terms of the total ester concentration, and k_e is the coefficient obtained by using the concentration of ester, a_e , which has been hydrolysed at the attainment of equilibrium.

In so far as (2) and (3) may be supposed to represent correctly the reaction velocity at different stages, the three values of dx/dt may be equated. From (1) and (2) we thus obtain

$$k_0/k_r = 1 - K_e x^2/w(a - x) \quad . \quad . \quad . \quad (4)$$

and from (1) and (3)

$$k_e/k_r = (a - x)\{1 - K_e x^2/w(a - x)\}/(a_e - x) \quad . \quad . \quad (5)$$

On the assumption that k_r is the true velocity coefficient of the hydrolytic reaction, the ratios k_0/k_r and k_e/k_r show to what extent equations (2) and (3) may be used in substitution for equation (1). When the ester concentration is small, *e.g.*, $a = 0.05$, the difference between the coefficients is not a matter of importance, but it may be readily shown that the difference is considerable for higher ester concentrations.

The comparison we have instituted has reference to the ester concentration used in our experiments, *viz.*, $a = 0.4$; under these conditions $w = 53.0$, and if $K_e = 4.0$, $a_e = 0.3886$, corresponding with 97.15% hydrolysis. The relevant numbers are shown in Table I, from which it is apparent that equation (2) yields a

TABLE I.
Comparison of Velocity Coefficients.

| | | | | | | | | |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| x | 0 | 0.05 | 0.1 | 0.15 | 0.2 | 0.25 | 0.3 | 0.35 |
| k_0/k_r | 1.0 | 0.999 | 0.997 | 0.993 | 0.985 | 0.969 | 0.932 | 0.815 |
| k_e/k_r | 1.029 | 1.033 | 1.037 | 1.040 | 1.044 | 1.048 | 1.052 | 1.055 |

“constant” which in the early stages of the reaction differs very little from the true coefficient k_r . On the other hand, equation (3) gives a “constant” which is very considerably greater than k_r , and such advantage as may be claimed for this equation is limited to the circumstance that the “constant” associated with it does not change very greatly even in the late stages of the reaction.

The relations disclosed by the above comparison have been of considerable assistance in deciding that equation (2) is to be preferred to (3) as a basis for the development of an integral formula to represent the earlier stages of the hydrolysis of ethyl acetate under the catalytic influence of acetic acid.

Results obtained in the study of the acetone-iodine reaction have shown that catalytic effects are produced by the undissociated acetic acid and the acetate ion as well as by the hydrogen ion, and if these are taken into account in the present case, the form assumed by equation (2) is

$$dx/dt = \{k_h[H^+] + k_a[A^-] + k_m[HA]\}w(a - x)$$

Experiments to be described in a subsequent paper show, however, that the coefficients k_a and k_m are very small, and that the terms $k_a[A^-]$ and $k_m[HA]$ can in general be neglected in comparison with $k_h[H^+]$ when acetic acid is used as catalyst in the absence of the corresponding salt. If b denotes the original concentration of the acetic acid, then $[H^+] = \sqrt{K(b + x - [H^+])} = \text{approx. } \sqrt{K(b + x)}$, and the previous equation becomes

$$dx/dt = k_h w \sqrt{K}(a - x)(b + x)^{\frac{1}{2}} \quad \dots \quad (6)$$

$$= k(a - x)(b + x)^{\frac{1}{2}} \quad \dots \quad (6a)$$

By substituting $y = (b + x)^{\frac{1}{2}}$, equation (6a) becomes

$$k \cdot dt = 2dy/(a + b - y^2)$$

which may be integrated by the method of partial fractions. We thus obtain

$$kt = \frac{1}{\sqrt{a+b}} \{ \log(\sqrt{a+b} + y) - \log(\sqrt{a+b} - y) \} + \text{constant},$$

and since $y = \sqrt{b}$ when $t = 0$

$$\text{constant} = - \frac{1}{\sqrt{a+b}} \{ \log(\sqrt{a+b} + \sqrt{b}) - \log(\sqrt{a+b} - \sqrt{b}) \}$$

Replacing y by $(b + x)^{\frac{1}{2}}$ and transposing, we obtain

$$k = \frac{1}{t\sqrt{a+b}} \left\{ \log \frac{\sqrt{a+b} + \sqrt{b+x}}{\sqrt{a+b} - \sqrt{b+x}} - \log \frac{\sqrt{a+b} + \sqrt{b}}{\sqrt{a+b} - \sqrt{b}} \right\} \quad (7)$$

This equation will be applied to experiments for which $a = 0.4$, and $b = 0.1$.

Preliminary observations under these conditions showed clearly that the reaction velocity increases in the early stages and this circumstance suggested a further analysis of equation (6a). By differentiation we obtain

$$dv/dx = \frac{1}{2}k(a - x)(b + x)^{-\frac{1}{2}} - k(b + x)^{\frac{1}{2}} \quad \dots \quad (8)$$

according to which the velocity passes through a maximum when $a - x = 2(b + x)$, *i.e.*, when $x = x_m = (a - 2b)/3$. If $a = nb$, x_m becomes $(n - 2)b/3$, and since this must be a positive quantity, it follows that a maximum velocity will only be obtained when the ester-acetic acid ratio is greater than 2. If $n =$ or < 2 , the velocity should fall continuously as the reaction proceeds.

In terms of n and b , the initial velocity v_0 is given by

$$v_0 = knb^3 \dots \dots \dots (9)$$

and the maximum velocity, v_m , by

$$v_m = 2k\{(n + 1)b/3\}^3 \dots \dots \dots (10)$$

whence for the ratio of maximum to initial velocity we obtain

$$v_m/v_0 = 2/n \cdot \{(n + 1)/3\}^3 \dots \dots \dots (11)$$

according to which this ratio depends only on n or a/b . Table II shows how the relative magnitude of the maximum velocity and the point at which it occurs depend on the value of n . The values of n , x_m , and v_m/v_0 are recorded in the first, second, and fourth horizontal lines; the third line gives the % of ester, $100x_m/a$, which has been hydrolysed when the velocity attains its maximum value.

TABLE II.

| | | | | | | |
|------------------|-----|-------|--------|------|--------|--------|
| n | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 10.0 |
| x_m | 0 | $b/3$ | $2b/3$ | b | $4b/3$ | $8b/3$ |
| $100x_m/a$ | 0 | 11.1 | 16.7 | 20.0 | 22.2 | 26.7 |
| v_m/v_0 | 1 | 1.03 | 1.075 | 1.13 | 1.19 | 1.40 |

EXPERIMENTAL.

The velocity measurements were made at 25°. The ethyl acetate was a fractionated research chemical which on saponification was found to contain 99.9% of ester. Preliminary observations showed that greatly increased accuracy could be obtained by the use of weight-volumetric methods and that this mode of procedure was essential in so far as the determination of the average speed at successive stages of the reaction was attempted.

In the recorded experiments, a 25 (or 10) c.c. sample of the ester solution was introduced into a weighed flask containing water and a measured quantity of phenolphthalein, the flask and its contents being re-weighed before and after the addition of the 0.1*N*-sodium hydroxide necessary to produce the tint accepted as an indication of the end-point. Using every precaution, it was found that titration results were reproducible within limits of ± 0.02 c.c. The influence of the titration error on the value of x varies with the progress of the reaction, but is in all cases such as

to warrant the belief that the accuracy of the analytical procedure was sufficient for the purpose of the inquiry.

Table III gives the detailed record of an experiment the data for which have been examined in reference to equation (7). Col. 1 gives the time in minutes, col. 2 the weight of solution titrated, and col. 3 the weight of standard alkali solution (0.0996*N*-NaOH) required. Col. 4 records the values of $(b + x)$ in mols. per litre, and col. 5 gives the values of k calculated from equation (7).

TABLE III.

$$a = 0.413; b = 0.0977.$$

| t (mins.). | Wt. of sol. titrated. | W. of standard alkali. | $b + x$. | $k \times 10^5$. |
|--------------|-----------------------|------------------------|-----------|-------------------|
| 1,645 | 24.934 | 24.462 | 0.1033 | 2.61 |
| 5,640 | 24.940 | 25.859 | 0.1172 | 2.63 |
| 9,970 | 24.943 | 29.337 | 0.1326 | 2.61 |
| 14,300 | 24.951 | 33.206 | 0.1481 | 2.61 |
| 17,160 | 10.006 | 14.875 | 0.1587 | 2.61 |
| 25,985 | 10.002 | 15.936 | 0.1902 | 2.59 |
| 33,005 | 10.002 | 20.139 | 0.2158 | 2.60 |
| 36,030 | 10.016 | 22.741 | 0.2262 | 2.59 |
| 43,120 | 9.993 | 25.169 | 0.2509 | 2.59 |
| 50,310 | 10.005 | 27.515 | 0.2739 | 2.59 |
| 64,675 | 9.999 | 31.797 | 0.3167 | (2.57) |
| 74,840 | 9.992 | 34.378 | 0.3427 | (2.56) |
| 84,860 | 9.987 | 36.710 | 0.3661 | (2.55) |
| 94,950 | 9.993 | 38.715 | 0.3859 | (2.54) |
| 106,870 | 9.985 | 40.760 | 0.4066 | (2.52) |

In accordance with the preceding analysis (compare Table I), the value of k would be expected to remain sensibly constant until about half of the original ester has been hydrolysed. As the figures in the last column of Table III indicate, this anticipation is fully realised within the limits of experimental error. The steady fall in the later (bracketed) values of k is quite in accordance with expectation.

If the experimental data for the later stages of the reaction are to be analysed with any degree of precision, it is essential that consideration should be given to the reverse reaction, but this does not necessarily imply the use of the complex integration formula (compare p. 2107). On the contrary, if the measurements of the reaction velocity are sufficiently accurate and the variations in the velocity are relatively small, the experimental results may be tested by comparing the observed average velocity for successive time intervals with the calculated velocity for the middle of each such interval. In so far as the variation of the velocity is concerned, the reaction investigated by us fulfils the stipulated requirement until the latest stages are reached, in that the effect of diminishing ester concentration is counteracted by the effect of

increasing concentration of the acetic acid. If $\bar{v} = \Delta x/\Delta t$ is the average velocity for an interval in which x increases from x_1 to x_2 , and $\bar{x} = (x_1 + x_2)/2$ represents the mean value of x , then in accordance with equation (6) we have

$$\bar{v} = k_h w \sqrt{K(a - \bar{x})(b + \bar{x})^2} - k'_h \bar{x} \sqrt{K(b + \bar{x})^2}$$

and since $k_h w \sqrt{K} = k$ and $k'_h = K_e k_h$

this may be written

$$\bar{v} = k\{(a - \bar{x})(b + \bar{x})^2 - K_e/w \cdot \bar{x}(b + \bar{x})^2\} . . \quad (12)$$

The application of equation (12) to the experimental data is shown in Table IV. Col. 1 gives the length of the time interval (Δt) between each successive pair of readings in Table III, col. 2 the mean concentration of the ester ($a - \bar{x}$), col. 3 the mean concentration of the acetic acid ($b + \bar{x}$), col. 4 the observed mean velocity, col. 5 the velocity calculated from equation (12) with $k = 2.61 \times 10^{-5}$ (see Table III), whilst col. 6 gives the values of k obtained by dividing the observed average velocity by $(a - \bar{x})(b + \bar{x})^2 - K_e/w \cdot \bar{x}(b + \bar{x})^2$.

TABLE IV.

| Δt (mins.). | $(a - \bar{x})$. | $(b + \bar{x})$. | $\bar{v} \cdot 10^6$ (obs.). | $\bar{v} \cdot 10^6$ (calc.). | $k \cdot 10^5$. |
|---------------------|-------------------|-------------------|------------------------------|-------------------------------|------------------|
| 1,645 | 0.4102 | 0.1005 | 3.45 | 3.39 | 2.65 |
| 3,995 | 0.4005 | 0.1102 | 3.48 | 3.47 | 2.62 |
| 4,330 | 0.3858 | 0.1249 | 3.56 | 3.56 | 2.61 |
| 4,330 | 0.3704 | 0.1403 | 3.58 | 3.62 | 2.57 |
| 2,860 | 0.3573 | 0.1534 | 3.70 | 3.65 | 2.64 |
| 8,825 | 0.3363 | 0.1744 | 3.57 | 3.65 | 2.55 |
| 7,020 | 0.3077 | 0.2030 | 3.65 | 3.60 | 2.65 |
| 3,025 | 0.2897 | 0.2210 | 3.44 | 3.52 | 2.55 |
| 7,090 | 0.2722 | 0.2385 | 3.48 | 3.44 | 2.64 |
| 7,190 | 0.2483 | 0.2634 | 3.20 | 3.28 | 2.55 |
| 14,455 | 0.2154 | 0.2953 | 2.96 | 2.99 | 2.58 |
| 10,075 | 0.1810 | 0.3297 | 2.58 | 2.62 | 2.56 |
| 10,020 | 0.1563 | 0.3544 | 2.34 | 2.32 | 2.63 |
| 10,090 | 0.1347 | 0.3760 | 1.96 | 2.03 | 2.52 |
| 11,920 | 0.1145 | 0.3962 | 1.74 | 1.73 | 2.62 |

In reference to the above table, it may be noted that the observations cover a period of 75 days, at the end of which about 75% of the ester had been hydrolysed. The original intention was to make the successive time intervals approximately equal, but various circumstances intervened to prevent the carrying out of this proposal. The close agreement of the observed and calculated velocities shows that the reaction proceeds throughout in accordance with the requirements of equation (12). This is further shown by the constancy of the k values in the last column.

The estimated probable error in the determination of the interval velocities is about 2% and this corresponds fairly well with the

deviations of the separate k values from the mean. The arithmetic mean of all the recorded numbers is $k = 2.60 \times 10^{-5}$, which is almost identical with the mean value of the coefficient derived from the application of the integration formula (7) to the first half of the reaction (see Table III).

In this connexion it may be noted that equation (12) involves the assumption that the hydrogen-ion concentration is given by $[H^+] = \sqrt{K(b + \bar{x})}$. If this were replaced by the more accurate value derived from $[H^+] = \sqrt{K(b + \bar{x} - [H^+])}$, the average value of k would be increased by about 0.4%. The use of the simpler expres-

FIG. 1.

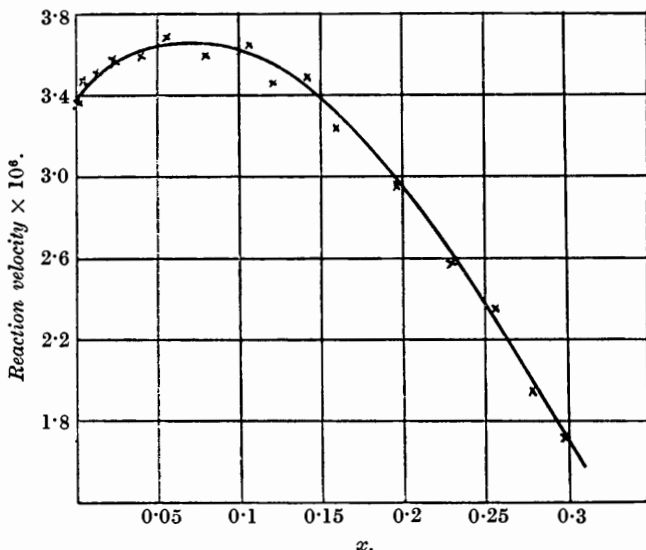


Diagram showing the variation of the reaction velocity with the proportion of ester hydrolysed.

sion is justified by the fact that the difference involved is probably within the limits of error of the mean value of k .

The observations recorded in Table IV do not actually give the initial velocity v_0 . To obtain this, measurements were made with solutions for which the initial concentrations of ester and acetic acid were so adjusted that $(a - \bar{x})$ and $(b + \bar{x})$ were equal to the initial values (a and b) in the experiment of Tables III and IV. The velocity derived in this way was $v_0 = 3.34 \times 10^{-5}$, which compares with the calculated value, $v_0 = 3.37 \times 10^{-5}$.

The course of the reaction may be clearly visualised with the aid of the diagram. The curve on this shows the variation of the

velocity as expressed by equation (12), whilst the points represent the measured average velocities for the successive time intervals. Equations (8) and (11) give $x_m = 0.072$ for the point at which the velocity reaches its maximum value and $v_m/v_0 = 1.087$ for the ratio of the maximum to the initial velocity. Although direct comparison between theory and experiment is not possible, it is apparent that these numbers are in general agreement with the observed course of the reaction.

Substituting $K = 1.85 \times 10^{-5}$ and $w = 53.2$ in the expression $k = k_h w \sqrt{K} = 2.61 \times 10^{-5}$, we obtain $k_h = 1.14 \times 10^{-4}$ as the value of the catalytic coefficient for the hydrogen ion in the hydrolysis of ethyl acetate at 25° .

Summary.

An examination has been made of the extent to which the neglect of the reverse reaction interferes with the derivation of true velocity coefficients in the process of ester hydrolysis. It is shown that the usual procedure does not yield the required coefficients unless the ester concentration is very small.

Accurate measurements of the rate of hydrolysis of ethyl acetate in presence of acetic acid have been made which permit of a direct comparison of the observed and calculated velocities at successive stages of the reaction.

Under the experimental conditions (ester, 0.4 molar; acetic acid, 0.1 molar), the velocity passes through a maximum in accordance with the theoretical predictions.

The value of the catalytic coefficient obtained for the hydrogen ion at 25° is $k_h = 1.14 \times 10^{-4}$.

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