CCCXXVII.—*Acid and Salt Effects in Catalysed Reactions. Part XI. The Hydrolysis of Ethyl Acetate and the Catalytic Catenary.*

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THE detailed study of the velocity of the acetone–iodine reaction in the presence of weak acids and the corresponding salts (see previous papers) has shown that catalytic effects of considerable magnitude are to be attributed to the undissociated acid and also to the acid anion. For various other reactions, evidence in favour of the catalytic activity of the undissociated acid has already been furnished by observations on the changes in reaction velocity which occur when the concentration of the acid is altered or when the corresponding salt is added, and an attempt has been made to explain the facts in terms of the so-called dual theory. According to later developments, the dual theory would seem to represent a very incomplete statement of the actual relations, and in the expectation that other reactions would show catalytic effects parallel with those observed in the action of iodine on acetone, measurements have been made of the rate of hydrolysis of ethyl acetate in presence of mixtures of acetic acid and sodium acetate. The mixtures used are represented by the general formula $c\text{HA} + x\text{MA}$, in which c is constant and x is variable.

Preliminary observations with $0{\cdot}1N$-acid solutions showed that, with a continually increasing salt content, the velocity falls at first to a minimum, and increases later in such a way that it can be represented as a linear function of x. Since for such a series of acid–salt mixtures the concentration of the hydroxyl ion is proportional to x, it was thought possible that the effects could be accounted for by the joint action of the hydrogen and hydroxyl ions. The reaction velocities calculated on this hypothesis are, however, much smaller than those observed, as may be illustrated by reference to the data for the most concentrated salt solution ($x = 2{\cdot}5$), for which the observed velocity is about 8 times as great as the calculated value. Furthermore, when the observed velocity was plotted against the p_{H} value of the solutions, it was found that the minimum velocity corresponds approximately with $p_{\text{H}} = 5{\cdot}1$. This represents a hydrogen-ion concentration which is much larger than would be expected on the assumption that the hydrogen and hydroxyl ions are the only active catalytic agents. The isocatalytic point on the $\overset{+}{\text{H}}\text{–}\overset{-}{\text{OH}}$ catenary is actually given by $[\overset{+}{\text{H}}]_i = \sqrt{k_{\text{OH}}K_w/k_h}$ and by substituting $k_{\text{OH}}/k_h = 1000$ and $K_w = 10^{-14}$, this equation yields a hydrogen-ion concentration which corresponds with $p_{\text{H}} = 5{\cdot}5$.

It thus appears that the observed minimum-velocity (*M.V.*) point differs in respect of both velocity and hydrogen-ion concentration from the isocatalytic point characteristic of the $\overset{+}{\mathrm{H}}$–$\overset{-}{\mathrm{O}}\mathrm{H}$ catenary, and this divergence led us to infer that the observed catalytic effects are connected with the catalytic activity of the undissociated acetic acid molecule and of the acetate anion. At the same time, the difference of 0·4 between the p_{H} values of the observed *M.V.* point and of the isocatalytic point on the $\overset{+}{\mathrm{H}}$–$\overset{-}{\mathrm{O}}\mathrm{H}$ catenary is small enough to suggest that the anionic catalytic effect will not be confined to the acetate ion, but will be shared by the acetate and hydroxyl ions. The relations involved in such circumstances have been already considered in connexion with the catalytic effects exhibited by acetate buffers (compare this vol., p. 1146).

In accordance with the above views, it follows that the initial value of the specific reaction velocity (velocity referred to unit concentration of ester) in the presence of catalysts of the series $0{\cdot}1\mathrm{CH_3{\cdot}CO_2H} + x\mathrm{CH_3{\cdot}CO_2Na}$ should be represented by the formula

$$\begin{aligned} v &= v_h + v_a + v_{\mathrm{OH}} + v_m \\ &= k_h[\overset{+}{\mathrm{H}}] + k_a[\overset{-}{\mathrm{A}}] + k_{\mathrm{OH}}[\overset{-}{\mathrm{O}}\mathrm{H}] + k_m[\mathrm{HA}] \quad . \quad . \quad (1) \end{aligned}$$

This equation may be reduced to the form $v = f[\overset{+}{\mathrm{H}}]$, but for the present purpose it will be applied directly to the experimental observations.

Attention may, in the first instance, be directed to the results for those solutions which contain relatively large proportions of salt. In such solutions, the catalytic effect of the hydrogen ion can be almost neglected, whilst the concentration, and therefore the catalytic effect, of the undissociated acetic acid is constant. The observed changes in reaction velocity are therefore attributable to variations in the magnitude of the catalytic effects which are represented by the second and third terms in equation (1). If the straight line which expresses the connexion between v and x is extrapolated to $x = 0$, it is obvious that the intercept on the ordinate affords a measure of $v_m = k_m[\mathrm{HA}] = 0{\cdot}1k_m$. The value thus obtained for k_m is $14{\cdot}5 \times 10^{-7}$.

Having thus determined k_m, the value of k_a may be derived from the observed velocity for any acid–salt mixture which falls on the linear portion of the v–x curve, in that k_a is the only remaining unknown quantity in equation (1). Rewriting this, we have

$$v_a = k_a x = v - k_h[\overset{+}{\mathrm{H}}] - k_{\mathrm{OH}}[\overset{-}{\mathrm{O}}\mathrm{H}] - k_m c,$$

and from the data for the mixture $0{\cdot}1CH_3{\cdot}CO_2H + 2{\cdot}0CH_3{\cdot}CO_2Na$, the value obtained for k_a is $2{\cdot}0 \times 10^{-7}$.

The four coefficients being known, it is now possible to apply equation (1) to the interpretation of the experimental results.

EXPERIMENTAL.

The observations, which were made at 25° with an ester concentration of 0·4 mol. per litre,* are concerned solely with the initial velocity of hydrolysis. The molar concentration of acetic acid (y) produced during a measured time interval (t) was determined by titration of 25 c.c. samples of the solution with 0·1N-sodium hydroxide. The value of y is based on an increase of 1—2 c.c. in the volume of standard alkali required to neutralise the test sample, and it is estimated that the error involved is not greater than ± 0·03 c.c. The ester hydrolysed during the period of observation thus corresponds with 1—2% of the total ester present, and in the region of the minimal velocities the time required for this is about 2 months. The specific velocity is given by $v = y/at$, where a is the initial ester concentration, and this velocity, it may be noted, is identical with the initial value of k in the equation $k = 1/t \,.\, \log_e a/(a - y)$ for a unimolecular reaction, in that this equation reduces to the form $k = y/at$ when y is small compared with a.

The results of the experiments are summarised in Table I. Col. 1 shows the molar concentration (x) of acetate, col. 2 the hydrogen-ion concentration calculated from $[\overset{+}{H}] = K(c - [\overset{+}{H}])/(x + [\overset{+}{H}])$, and from this the values of $[\overset{-}{A}]$, $[\overset{-}{OH}]$, and [HA] are derived. Cols. 3—6 give the values of v_h, v_a, v_{OH}, and v_m, respectively, col. 7 the total calculated velocity $v = v_h + v_a + v_{OH} + v_m$, and col. 8 the corresponding observed specific velocity. The values employed for the various velocity coefficients are: $k_h = 6{\cdot}1 + 10^{-3}$,† $k_a = 2{\cdot}0 \times 10^{-7}$, $k_{OH} = 6{\cdot}5$, and $k_m = 14{\cdot}5 \times 10^{-7}$; for the ionisation constant of acetic acid $K = 1{\cdot}85 \times 10^{-5}$, and for the ionic product of water $K_w = 10^{-14}$.

With reference to Table I it may be noted that the catalytic effects produced by the acetate and hydroxyl ions are in a constant ratio, the value of which is given by $v_a/v_{OH} = k_aKc/k_{OH}K_w = 5{\cdot}7$. The general agreement between the numbers in the last two columns affords substantial evidence that the observed catalytic effects are

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* On account of "salting-out," this was reduced to 0·2 mol./litre in the case of the three most concentrated salt solutions.

† This value is based on the results obtained in the detailed investigation of the hydrolysis of ethyl acetate under the catalytic influence of acetic acid (compare Dawson and Lowson, this vol., p. 2107).

TABLE I.

Hydrolysis of ethyl acetate at 25°. Catalyst: $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$.

						$v\,.\,10^7$.	
x.	$[\overset{+}{\mathrm{H}}]\,.\,10^5$.	$v_h\,.\,10^7$.	$v_a\,.\,10^7$.	$v_{\mathrm{OH}}\,.\,10^7$.	$v_m\,.\,10^7$.	Calc.	Obs.
0	135	82·3	—	—	1·43	83·7	81·6
0·005	34·5	21·0	0·01	—	1·45	22·5	23·0
0·015	12·2	7·45	0·03	—	1·45	8·9	9·1
0·03	6·15	3·75	0·06	0·01	1·45	5·3	5·2
0·05	3·7	2·25	0·10	0·02	1·45	3·8	4·2
0·07	2·65	1·62	0·14	0·03	1·45	3·25	3·3
0·10	1·85	1·13	0·20	0·04	1·45	2·8	2·5
0·20	0·92	0·56	0·40	0·07	1·45	2·5	2·5
0·35	0·53	0·32	0·70	0·12	1·45	2·6	2·45
0·50	0·37	0·22	1·00	0·17	1·45	2·85	3·0
1·0	0·185	0·11	2·00	0·35	1·45	3·9	3·7
1·5	0·123	0·07	3·00	0·52	1·45	5·05	5·5
2·0	0·092	0·05	4·00	0·70	1·45	6·2	6·2
2·5	0·074	0·04	5·00	0·88	1·45	7·4	7·6

due to the combined action of the hydrogen, acetate, and hydroxyl ions and of the undissociated acetic acid molecule.

In accordance with relations derived previously (Dawson and Dean, J., 1926, 2872; Dawson, this vol., p. 1146), the plot of the reaction velocity against p_{H} yields a symmetrical curve of catenary type. This curve is characterised by a minimum (isocatalytic) point, the hydrogen-ion concentration of which is given by

$$[\overset{+}{\mathrm{H}}]_i = \sqrt{(k_aKc + k_{\mathrm{OH}}K_w)/k_h}$$

and the corresponding minimum reaction velocity by

$$v_i = 2\sqrt{k_h(k_aKc + k_{\mathrm{OH}}K_w)} + k_mc,$$

if k_m be neglected in comparison with k_h.

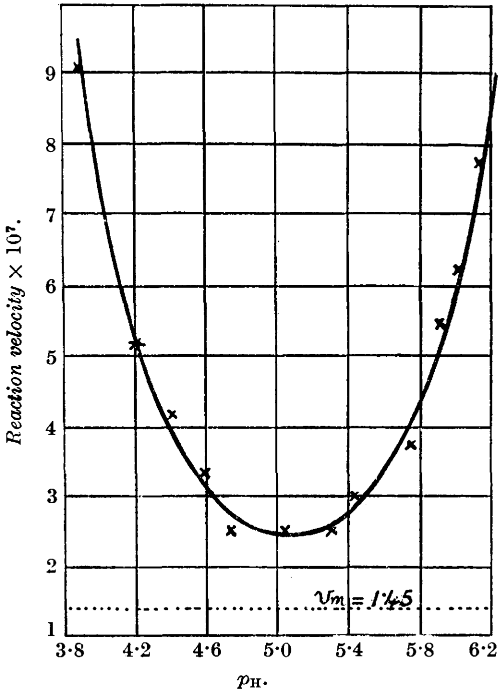
By substitution of the values for the various constants, these equations give $[\overset{+}{\mathrm{H}}]_i = 8{\cdot}4 \times 10^{-6}$, or $(p_{\mathrm{H}})_i = 5{\cdot}07$, and $v_i = 2{\cdot}48 \times 10^{-7}$.

The diagram shows a catenary curve which has been drawn to show the connexion between the observed reaction velocities and the p_{H} values of the solutions. These p_{H} values are those derived on the assumption that the mass law is applicable to the ionisation of acetic acid and that the acetate is completely ionised. The co-ordinates of the apex of this catenary are obviously in close agreement with the above values of v_i and $(p_{\mathrm{H}})_i$.

The dotted horizontal line represents the velocity v_m due to the undissociated acetic acid. This may be regarded as the base line for the u—p_{H} curve, where u is the ionic reaction velocity.

According to the procedure adopted on p. 2445 for the evaluation of the coefficients k_m and k_a, the former was derived by extrapolation of the linear portion of the v–x curve, whilst the latter was obtained from the slope of this line. Since the slope is determined by the joint action of the acetate and hydroxyl ions, a knowledge of k_{OH} is implied, and when the value of this coefficient is not known, other methods must be used for the derivation of k_a. These need not be described in the present paper, but reference may appropriately be made to an alternative method for the determination of k_m.

FIG. 1.



Catalytic activity of $0{\cdot}1N{\cdot}CH_3{\cdot}CO_2H + xN{\cdot}CH_3{\cdot}CO_2Na$ *in the hydrolysis of ethyl acetate. Reaction velocity* ($v \times 10^7$) *plotted against* p_H.

If the hydrogen-ion concentrations of solutions of the constant-acid series are expressed in terms of the hydrogen-ion concentration of the isocatalytic mixture, such that $n = [\overset{+}{H}]/[\overset{+}{H}]_i$, the equation for the reaction velocity may be written

$$v = k_h[\overset{+}{H}]_i(n + 1/n) + k_m c$$

and for larger values of n this becomes

$$v = nk_h[\overset{+}{H}]_i + k_m c \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The corresponding equation for the minimum velocity is

$$v_i = 2k_h[\overset{+}{\mathrm{H}}]_i + k_m c \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Multiplying (2) by 2 and (3) by n, we obtain by subtraction

$$k_m = (nv_i - 2v)/(n - 2)c \quad . \quad . \quad . \quad . \quad (4)$$

The use of equation (4) for the determination of k_m presumes a knowledge of the isocatalytic data, but does not entail measurements of reaction velocity for solutions which contain a much larger proportion of salt than that which is present in the isocatalytic mixture. In this respect, the method is very different from the extrapolation method, and since for various reasons the experimental realisation of the linear portion of the v–x curve is not always possible, the method represented by equation (4) may frequently be found to be useful for the determination of k_m.

Its application in the present case is illustrated by Table II, in which the relevant numbers for the solutions containing relatively small quantities of salt are recorded.

TABLE II.

$c = 0{\cdot}1.\quad [\overset{+}{\mathrm{H}}]_i = 8{\cdot}4 \times 10^{-6},\ v_i = 2{\cdot}5 \times 10^{-7}.$

x.	$[\overset{+}{\mathrm{H}}] . 10^5$.	n.	$v . 10^7$.	$k_m . 10^7$.
0	135	159	81·6	15·0
0·005	34·5	40·5	23·1	14·3
0·015	12·2	14·4	9·1	14·4
0·03	6·15	7·3	5·2	14·8

In spite of the wide variation in the value of the " reduced " hydrogen-ion concentration (n), the numbers under k_m are remarkably concordant, and this may be regarded as further evidence in support of the validity of the general theoretical considerations on which the method of interpreting the results is based. According to this, the catalytic effects associated with acetic acid and its salts in the hydrolysis of ethyl acetate are very similar to those previously met with in the case of the acetone–iodine reaction. The main difference is attributable to the fact that the ratios k_m/k_h and k_a/k_h are much larger for the latter reaction than for the ester hydrolysis. This is also true for the ratio k_{OH}/k_h. The actual values of the ratios are shown in Table III.

TABLE III.

Reaction.	$10^5 \times k_m/k_h$.	$10^5 \times k_a/k_h$.	$10^{-3} \times k_{\mathrm{OH}}/k_h$.	$10^{-6} \times k_{\mathrm{OH}}/k_a$.
(A) Acetone–iodine ...	320	970	43	4·4
(B) Hydrolysis of ethyl acetate ...	24	3·3	1·05	32

According to the above figures k_a/k_h is about 300 times as great for reaction A as for reaction B. This is mainly responsible for the fact that the amount of acetate which must be added to 0·1*N*-acetic acid to reduce the reaction velocity to a minimum is nearly 20 times as great in B as it is in A. On the other hand, k_{OH}/k_a is about 7 times as great in B as it is in A. This explains why the anionic catalytic effect in B is shared by the acetate and hydroxyl ions, although the corresponding effect in A is almost entirely due to the acetate ion. That the nature of the catalysed reaction affects the relative activities of the undissociated acid and the corresponding anion is evident from the value of the ratio k_m/k_a; this is 0·33 in reaction A and 7·2 in reaction B.

Catalytic Effects for Different Reactions and the General Catenary.—Since the catalytic effects associated with the two reactions which have been compared are in agreement with the requirements of the general catalytic catenary (compare this vol., p. 213), according to which the reduced ionic velocity $r = u/u_i$ is connected with the reduced hydrogen-ion concentration, $n = [\overset{+}{\text{H}}]/[\overset{+}{\text{H}}]_i$, and the reduced p_{H} value, $\Delta p_{\text{H}} = \log_{10} n$, by the equations

$$r = \tfrac{1}{2}(n + 1/n) = \tfrac{1}{2}(10^{\Delta p_{\text{H}}} + 10^{-\Delta p_{\text{H}}})$$

these reduced quantities should afford a basis for the comparison of the ionic catalytic effects which are peculiar to a given acid in a series of different reactions. It has, in fact, been shown (this vol., p. 756) that the reduced hydrogen-ion concentration (n_0) of a solution of the pure acid and the corresponding reduced ionic velocity (r_0) are determined solely by the relative magnitudes of the catalytic coefficients and are independent of the concentration and therefore of the degree of ionisation of the acid. The value of n_0 (or r_0) determines the position which must be assigned to a given pure acid on the general catalytic catenary, and this position obviously varies with the nature of the catalysed reaction. For acetic acid, the value of n_0 is 10 when the acid catalyses the acetone–iodine reaction, and about 175 when it catalyses the hydrolysis of ethyl acetate. Such wide variations in n_0 do not, of course, affect the validity of the relations which find expression in the equation of the general catalytic catenary, but they serve to show that the catalytic activity of a given pure acid expressed in terms of that of the corresponding *M.V.* mixture varies very considerably with the nature of the catalysed reaction.

Summary.

Measurements have been made of the catalysing power of acetic acid–sodium acetate mixtures in the hydrolysis of ethyl acetate.

For a fixed concentration of acid, the addition of salt first reduces the velocity, which passes through a minimum, and then increases it according to a linear formula.

The observed reaction velocities can be explained in terms of the joint catalytic effects produced individually by the hydrogen, acetate, and hydroxyl ions and by the undissociated acetic acid.

The connexion between the reaction velocity and the p_H value of the solution is represented very closely by a catenary curve.

The ratios k_a/k_h and k_m/k_h are much smaller for the hydrolysis of ethyl acetate than for the acetone–iodine reaction, and the catalytic catenary is of the compound type.

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