CLIX.—*Acid and Salt Effects in Catalysed Reactions. Part VIII. The Determination of Hydrolytic Velocity Coefficients from Isocatalytic Data. Reaction Velocities in Buffer Solutions and Compound Catalytic Catenaries.*

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IN accordance with the theory outlined in previous papers (see, *e.g.*, this vol., p. 461), the velocity of hydrolytic reactions * has a minimum value when the hydrogen-ion concentration is that given by the equation

$$[H^+]_i = \sqrt{k_{OH}K_w/k_h} \quad . \quad . \quad . \quad . \quad (1)$$

At this point the partial velocities due respectively to the hydrogen ion and the hydroxyl ion are equal, and the total ionic reaction velocity is given by

$$u_i = 2\sqrt{k_h k_{OH} K_w} \quad . \quad . \quad . \quad . \quad (2)$$

From these equations, the isocatalytic data $[H^+]_i$ and u_i can be calculated if the coefficients k_h and k_{OH} are known; or, alternatively, the derived equations

$$2k_h = u_i/[H^+]_i \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2k_{OH} = u_i[H^+]_i/K_w \quad . \quad . \quad . \quad . \quad (4)$$

and

$$k_{OH}/k_h = [H^+]_i^2/K_w \quad . \quad . \quad . \quad . \quad (5)$$

enable the converse calculations to be made. It is apparent that the derivation of k_{OH} or k_{OH}/k_h involves a knowledge of the ionisation product of the solvent, but that this is not required for the determination of k_h.

* The term hydrolytic reaction is used in this paper for any reaction which is catalysed by both the hydrogen and the hydroxyl ion.

The consideration of hydrolytic reactions from the point of view of the experimental measurement of the four quantities k_h, k_{OH}, $[H^+]_i$ and u_i is a matter of some interest. For those reactions in which undissociated water molecules take no measurable part, the ionic reaction velocity u may be identified with the actually measured velocity (v) and it is with reactions of this type that the present paper is primarily concerned. The procedure followed in the determination of k_h and k_{OH} is well known, and it need only be mentioned that attempts to measure v_i and $[H^+]_i$ have been made for the most part by the use of buffer solutions of varying p_H value.

In general, it is not possible to determine each of the four quantities k_h, k_{OH}, v_i, and $[H^+]_i$ by direct measurement, but the hydrolysis of aliphatic esters affords instances in which this may be readily accomplished, so far as the time factor is concerned. When the velocities of reaction, as measured by k_h and k_{OH}, are very much smaller, the direct measurement of v_i and $[H^+]_i$ may be attended with difficulties, as, for instance, in the case of the hydrolysis of aromatic amides at the ordinary temperature.

For some reactions, the relations may be such that only one of the velocity coefficients can be measured in the ordinary way. If, for instance, the ratio k_{OH}/k_h is of the order of 10^5, it is obvious that only one of the coefficients can be obtained directly from experiment. Quite apart from the difference in the order of magnitude of the coefficients, the transition from acid to alkaline solution may be complicated by the incidence of other reactions, concurrent or consecutive, which interfere with the measurement of the reaction velocity in question. Such complications occur in the acetone–iodine reaction, for which the value of k_h can be determined quite conveniently, but since the ratio k_{OH}/k_h is about 40,000, it is apparent that the direct measurement of k_{OH} would not be a simple matter even under the most favourable conditions. In actual fact, the measurement is precluded by the circumstance that subsequent reactions, leading to the production of iodoform, effectively mask the relations which characterise the primary stage of the acetone–iodine reaction in solutions of $p_H > 6$. In this particular instance, however, it has been found possible to determine the value of $[H^+]_i$ from observations on the velocity of the autocatalysed reaction (Dawson and Powis, J., 1912, **101**, 1503; Dawson, this vol., p. 458), and by combining this with k_h, the values of v_i and k_{OH} may be derived from equations (3) and (4).

Other hydrolytic reactions are distinguished by the circumstance that the values of k_h and k_{OH} are both so large that neither can be determined directly. It is not improbable that many of the reactions associated with the phenomena of tautomerism, pseudo-acidity, etc.,

afford examples which belong to this group. In such cases, it may sometimes be possible to obtain the velocity coefficients from the measurements of v_i and $[H^+]_i$.

Reactions in Buffer Solutions.

Since the use of buffer solutions serves to provide the stabilised p_H conditions which are necessary for the determination of v_i and $[H^+]_i$ in the case of hydrolytic reactions, it is necessary to examine critically the factors which are involved in the employment of such solutions for this purpose. In the light of the results which have been described previously (Dawson and Carter, J., 1926, 2282), it cannot be assumed that the catalytic effect of the acid and salt in the buffer solution is negligible. If, for instance, the solution used is an acetate buffer of p_H 5, in which the total acetate concentration is $0.02M$, the concentrations of the constituents for which catalytic activity has been demonstrated are $[H^+] = 10^{-5}$, $[OH^-] = 10^{-9}$, $[HA] = 6 \times 10^{-3}$, and $[A^-] = 14 \times 10^{-3}$. In other words, the concentrations of the acetic acid and of the acetate ion are, respectively, 6×10^6 and 14×10^6 times that of the hydroxyl ion. In such circumstances, the possible catalytic action of buffer constituents, other than the hydrogen and hydroxyl ions, cannot be ignored. It may, in fact, be shown that the use of buffer mixtures does not in general yield the isocatalytic data which are characteristic of the H^+–OH^- catenary.

For the sake of simplicity it will be assumed that the buffer mixture consists of a weak acid HA and its corresponding salt, and that the variation of p_H is brought about by altering the concentration of the salt whilst the concentration of the acid (c) is kept constant. If the acid is not too weak, and its concentration not too small, the use of such a series of buffer solutions would give a point of minimum velocity characterised by values of $[H^+]_i$ and v_i given by the equations

$$[H^+]_i = \sqrt{k_a Kc/(k_h - k_m)} \quad . \quad . \quad . \quad (6)$$

and
$$v_i = 2\sqrt{(k_h - k_m)k_a Kc} + k_m c \quad . \quad . \quad (7)$$

On the other hand, the isocatalytic data corresponding with the joint action of the hydrogen and hydroxyl ions are given by equations (1) and (2). In general, there will be a considerable difference between the two pairs of isocatalytic data. For the weaker acids which are commonly used in the preparation of buffer mixtures, k_m can be neglected in comparison with k_h and the difference between the two hydrogen-ion concentrations is essentially determined by the value of the ratio $k_a Kc/k_{OH} K_w$. The difference would seem to disappear when $c = k_{OH} K_w/k_a K$. If the concentration of the acid

has this value, the $M.V.$ point actually realised does not correspond, however, with equations (1) and (2), i.e., with the H^+–OH^- catenary, but minimum velocity is attained at a greater hydrogen-ion concentration, which indeed is characteristic of a catenary curve for which the anionic catalytic effect is shared by the acid ions A^- and OH^-. This catenary may conveniently be described as a compound catenary.

The Compound Catenary.—Under conditions in which the total catalytic effect of the negative ions is shared by A^- and OH^-, the equation for the velocity of reaction may be written

$$v = k_h[H^+] + k_a[A^-] + k_{OH}[OH^-] + k_m[HA] + k_w[H_2O] \quad . \quad (8)$$

Since $[A^-] = K(c-[H^+])/[H^+]$ and $[OH^-] = K_w/[H^+]$, equation (8) may be put in the form

$$v = (k_h - k_m)[H^+] + (k_aKc + k_{OH}K_w)/[H^+] + k_mc + k_wc_w - k_aK \quad (9)$$

and if the concentration (c) of the acid HA is constant, it is evident that the reaction velocity passes through a minimum when

$$[H^+] = [H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/(k_h - k_m)} \quad . \quad (10)$$

and by substitution in (9) the minimum velocity is given by

$$v_i = 2\sqrt{(k_h - k_m)(k_aKc + k_{OH}K_w)} + k_mc + k_wc_w \quad (11)$$

if the negligibly small term k_aK be left out of account. The relations involved are of exactly the same kind as those which have been already described in connexion with the catalytic activity of acid–salt mixtures of the type $cHA + xMA$, and it is obvious that the total catalytic effects are such that the reaction velocity, in its dependence on p_H, can be represented by a catenary curve symmetrical with reference to the point defined by equations (10) and (11).

These compound catenaries form a continuous series limited on the one side by the H^+–OH^- catenary, and on the other by the simple catenaries which correspond with the acid–salt mixtures of the type $cHA + xMA$, for which the effect of the hydroxyl ion can be ignored. The relation between the hydrogen-ion concentrations $[H^+]_i'$ characteristic of the $M.V.$ points on the compound catenaries and the hydrogen-ion concentration $[H^+]_i$ of the $M.V.$ point on the H^+–OH^- catenary is given by

$$[H^+]_i'/[H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/k_{OH}K_w}$$

or
$$(p_H)_i - (p_H)_i' = \tfrac{1}{2}\log m \quad . \quad . \quad . \quad . \quad (12)$$

where $m = (k_aKc + k_{OH}K_w)/k_{OH}K_w$.

The numerical relations involved may be illustrated by reference to the acetone–iodine reaction for which the requisite data are

available.   At 25° and an acetone concentration of 20 c.c. per litre, $k_{OH}K_w = 2 \cdot 0 \times 10^{-13}$, and for acetic acid $k_aKc = 832 \times 10^{-13}c$. In Table I are shown the values of c, $k_aKc \times 10^{13}$, $\sqrt{m}$, and $(p_H)_i - (p_H)_i'$.

TABLE I.

c	0	0·0001	0·0002	0·0005	0·001
$k_aKc \times 10^{13}$	0	0·08	0·16	0·42	0·83
$\sqrt{m}$	1·0	1·02	1·04	1·10	1·19
$(p_H)_i - (p_H)_i'$	0	0·01	0·02	0·04	0·08
c	0·002	0·005	0·01	0·02	0·05
$k_aKc \times 10^{13}$	1·66	4·15	8·3	16·1	41·6
$\sqrt{m}$	1·35	1·75	2·27	3·05	4·67
$(p_H)_i - (p_H)_i'$	0·13	0·24	0·36	0·48	0·67

When the concentration of the acetic acid reaches $0 \cdot 05N$, the catalytic effect of the hydroxyl ion can be almost neglected and the end of the series of compound catenaries may be said to have been reached.   The non-interference of the H^+–A^- and H^+–OH^- catenaries may therefore be said to require that the difference in the p_H values of the $M.V.$ points should not be less than about $0 \cdot 7$ p_H unit.

The gradual displacement of the $M.V.$ point in passing from the H^+–OH^- catenary to the simple H^+–A^- catenaries is possibly best illustrated by reference to the exponential curves which represent the catalytic effect of the hydrogen ion on the one hand and the combined catalytic effect of the anions on the other.   In adopting this method of comparing the relations, it is assumed that the acid HA is weak and that the coefficient k_m can be neglected in comparison with k_h.   In these circumstances, the partial ionic reaction velocities are given by

$$v_h = k_h \cdot 10^{-p_H} \text{ and } v_a = (k_aKc + k_{OH}K_w)10^{p_H}$$

The curve for v_h and a group of v_a curves for acetic acid concentrations ranging from $c = 0$ to $c = 0 \cdot 05N$ are shown in the diagram and it need only be pointed out that the p_H values of the points of intersection of the v_h curve with the several v_a curves are identical with the $M.V.$ points of the corresponding catenaries under the conditions which are here postulated.

In regard to the compound catenaries, it should be added that these conform to the requirements of the general catenary in exactly the same way as the simple catenaries.   The applicability of the general catalytic catenary is thus further extended to include ionic catalytic effects in which the contribution of the negative ions is shared by anions derived respectively from the solvent and from the acid–salt mixture present in the solution.

The bearing of the above results on the use of buffer mixtures for the study of the velocity of hydrolytic reactions is obvious. The minimum velocities observed under such conditions are larger, and the p_H values smaller than those which would correspond with the $M.V.$ point characteristic of the undisturbed action of the hydrogen and hydroxyl ions. In this connexion, it may be noted that since the buffer acid is weak (k_m negligible in comparison with k_h), equations (10) and (11) give $u_i/[\mathrm{H}^+]_i = 2k_h$, which is identical with

FIG. 1.
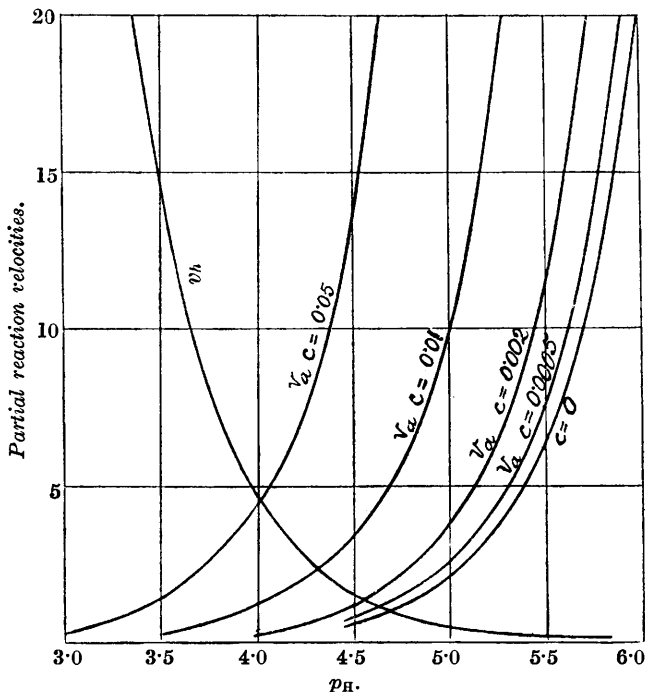
Plot of partial velocities due to the hydrogen ion (v_h) and the acetate + hydroxyl ions (v_a) against p_H.

equation (3). It must be remembered, however, that the ionic reaction velocity u_i is not directly measurable. On the assumption that the undissociated water molecules have no measurable activity, the ionic reaction velocity is derived from $u_i = v_i - k_m c$, which requires a knowledge of the catalytic activity of the undissociated buffer acid.

In the circumstances outlined above, it is apparent that the observations made by Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69; 1925, **145**, 1) and Bolin (*ibid.*, 1925, **143**, 201) do not yield either

$(p_H)_i$ values or minimum reaction velocities which can be utilised directly for the derivation of k_h or k_{OH} with any approach to accuracy.

Notwithstanding the approximate character of the $(p_H)_i$ values recorded by Karlsson and Bolin, their data serve to show that the ratio k_{OH}/k_h varies enormously with the nature of the catalysed reaction. The values obtained from the logarithmic equivalent of equation (5), *viz.*,

$$\log k_{OH}/k_h = -\log K_w - 2(p_H)_i,$$

are shown in the fifth column of Table II. Column 1 shows the hydrolyte, col. 2 the temperature of the velocity measurements, col. 3 the ionisation product of water at this temperature, and col. 4 the $(p_H)_i$ values recorded by the above observers.

TABLE II.

Hydrolyte.	Temp.	$K_w \times 10^{14}$.	$(p_H)_i$.	k_{OH}/k_h.
Methyl acetate	25°	1·0	5·15	5,000
Ethyl acetate	25	1·0	5·36	1,900
Glycerol monoacetate	25	1·0	5·0	10,000
Ethyl chloroacetate	20	0·8	4·8	32,000
Ethyl formate	20	0·8	4·65	63,000
Ethyl aminoacetate	20	0·8	3·5	12×10^6
Acetanilide	40	4·0	5·80	63
Benzamide	80	25	6·2	1·6

The value of $(p_H)_i$ given for methyl acetate is that derived by Karlsson (*loc. cit.*, p. 31) from the plot of the logarithm of the observed velocity against p_H; this would seem to be more accurate than the lower value indicated by the v–p_H curve.

For the first five hydrolytes, for which the recorded $(p_H)_i$ values were obtained directly from experiments with buffer solutions, it is probable that the values of k_{OH}/k_h are too large on account of the disturbing influence of the buffer acid and salt. Some indication of the magnitude of this disturbance is obtained when it is pointed out that the correct value of k_{OH}/k_h for ethyl acetate is about 1000. The $(p_H)_i$ values recorded by Bolin for acetanilide and benzamide were derived on the assumption that the acid and alkaline branches of the v–p_H curve are symmetrical with respect to the point of minimum reaction velocity. This empirical assumption is entirely in agreement with the theoretical conclusion reached by Dawson and Dean (J., 1926, 2872) that the p_H value of the $M.V.$ point is the arithmetic mean of the p_H values for pairs of solutions of the series cHA + xMA which have the same catalytic power.

The application of the isocatalytic method to the systematic determination of the ratio k_{OH}/k_h by the rational use of buffer

solutions should make it possible to extend the number of reactions for which this ratio can be derived and thus provide material for the investigation of the question of the mode of action of the hydrogen and hydroxyl ions as catalytic agents in so-called hydrolytic reactions.

Summary.

It is shown that the velocity coefficients k_h and k_{OH} can be derived from the isocatalytic data v_i and $[H^+]_i$.

Approximate values of v_i and $[H^+]_i$ may be obtained by the use of buffer solutions, but the experimental data, which indicate that k_{OH}/k_h varies with the hydrolyte between very wide limits, must be corrected for the catalytic effects which are produced by constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

The curves obtained by plotting the reaction velocity against the p_H value of a series of buffer solutions, in which the concentration of the acid is constant, are catenary in type. These catenary curves are compound in character in that the anionic catalytic effect is shared by the hydroxyl ion and by the anion of the acid in the buffer mixture.

The compound catenaries form a continuous series limited on the one hand by the H^+–OH^- catenary, and on the other by the simple H^+–A^- catenaries corresponding with the mixtures $cHA + xMA$.

The compound catenaries conform to the requirements of the general catalytic catenary, the application of which is thus extended to include anionic catalytic effects which are shared by the hydroxyl ion with other acid anions.