LXX.—*Acid and Salt Effects in Catalysed Reactions. Part XII. The Water Catenary* (H^+–H_2O–OH^-) *in the Iodination of Acetone.*

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SINCE the publication of the first of this series of papers (Dawson and Carter, J., 1926, 2282), in which evidence was brought forward to show that catalytic effects are produced by negatively charged anions and by electrically neutral molecules as well as by positively charged "hydrogen" (oxonium) ions, the existence of similar effects has been conclusively demonstrated in other catalysed reactions. Studies of the mutarotation of glucose by Brönsted and Guggenheim (*J. Amer. Chem. Soc.*, 1927, **49**, 2554) and by Lowry and Smith (J., 1927, 2539) have established the activity of anions and molecules in this reaction, and have also shown that catalytic activity must be attributed to other complex positive ions of the oxonium type, such as $NH^{\bullet}_4$, $NH_3R^{\bullet}$, etc. It seems probable that the activity of all such ions and molecules depends on their acid or basic character, that is to say, on their ability to act as proton donators or proton acceptors.

From an examination of the data for a large number of hydrolytic reactions, Skrabal (*Z. Elektrochem.*, 1927, **33**, 322) concludes that the very wide differences which are exhibited by such reactions towards changes in the concentration of the hydrogen ion can be satisfactorily interpreted in terms of the joint action of the hydrogen ion, hydroxyl ion, and undissociated water when the large variations in the relative values of the respective catalytic coefficients are taken into account. Skrabal has also shown the existence of symmetry in the curve which is obtained by plotting the logarithm of the reaction velocity against p_H. This symmetry is a particular and necessary consequence of the more general relations which have been shown by one of us to apply to the catalytic effects produced by any weak acid in virtue of the activity of the positive ions, negative ions, and undissociated molecules.

For acid–salt mixtures of the type $c\text{HA} + x\text{MA}$, where c is constant and x is variable, the plot of the reaction velocity against the logarithm of the hydrogen-ion concentration or p_H gives a catenary curve. The salt-free solution of the acid represents the limiting member of such a series of mixtures, but the catenary curve is not actually limited by this circumstance, for the addition of a completely ionised acid in which the hydrogen ion is associated with a catalytically inert anion, should obviously be equivalent to the addition of the salt MA, in which the active anion is associated with a catalytically inert metallic cation. The symbol $(\text{H}^+\text{–HA–A}^-)_c$ may be conveniently used when reference has to be made to the catenary curve which corresponds with the acid HA at the concentration represented by c. If the acid in question is water, the catalytic effects correspond with the water catenary, $\text{H}^+\text{–H}_2\text{O–OH}^-$.

The usual conditions under which catalytic observations are made with the strong acids and bases correspond with the upper reaches of the water catenary, and the data so obtained may be taken as an accurate measure of the catalytic activity of the hydrogen ion or of the hydroxyl ion if the activity of the undissociated water is negligibly small. When, however, the catalysed reaction involves the formation or disappearance of acid or basic substances, the changes thereby produced in the hydrogen-ion concentration are such as to prevent the realisation of those conditions which are essential for the direct investigation of the lower portion of the water catenary. Constancy of p_H may be obtained by the use of buffer solutions, and it has been shown (J., 1927, 1290) that the velocity which is characteristic of the minimum-velocity (*M.V.*) point on the water catenary may be derived indirectly from the minimum velocity which is shown by series of buffer mixtures for which the concentration of the buffer acid or the concentration of the buffer salt is constant. In the application of this method, it is, however, necessary to know the values of the catalytic coefficients for both the undissociated acid and the acid anion in the buffer mixture.

In the present paper, an alternative method of procedure is described which has the advantage of great simplicity, and furthermore permits of the determination of the velocity which is characteristic of any desired point on the water catenary. This velocity is given by the equation

$$v_0 = v_h + v_{\mathrm{OH}} + v_w = k_h[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + k_w[\mathrm{H_2O}] \quad . \quad (1)$$

or since $[\mathrm{H}^+].[\mathrm{OH}^-] = K_w$ and $[\mathrm{H_2O}] = 55$

$$v_0 = k_h[\mathrm{H}^+] + k_{\mathrm{OH}}K_w/[\mathrm{H}^+] + 55k_w \quad . \quad . \quad . \quad (1a)$$

according to which the velocity is determined by the hydrogen-ion concentration. If this hydrogen-ion concentration is produced by the use of a buffer mixture $c\mathrm{HA} + s\mathrm{MA}$, in which the ratio c/s is constant $= q$, the value of $[\mathrm{H}^+]$ is given by

$$[\mathrm{H}^+] = K(c - [\mathrm{H}^+])/(s + [\mathrm{H}^+]),$$

and if c and s are not too small, this is equal to Kq. For such a buffered solution, the reaction velocity is given by

$$\begin{aligned} v &= k_h[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + k_w[\mathrm{H_2O}] + k_m c + k_a s \\ &= v_0 + k_m c + k_a s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

which may be written in the form

$$v = v_0 + (k_a + qk_m)s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

or

$$v = v_0 + (k_m + k_a/q)c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

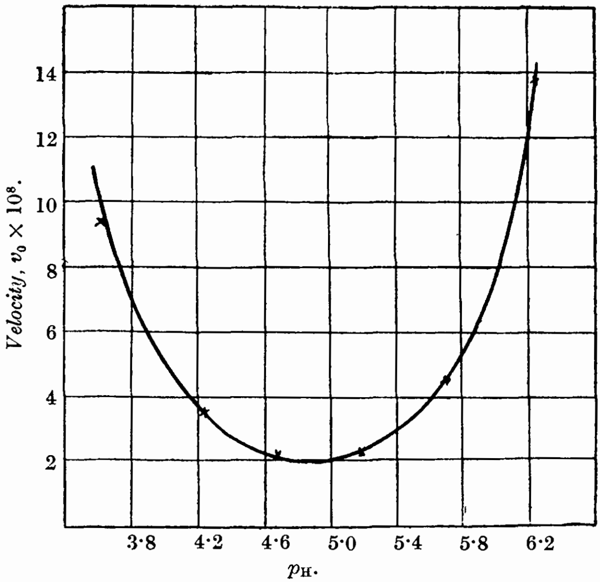
according to which the velocity is a linear function of the concentration of the salt or the acid in the buffer mixtures. When the straight line for a series of buffers with a fixed value of q is extrapolated to zero salt (or acid) concentration, we obtain the velocity v_0 which is characteristic of the isohydric point on the water catenary, and by variation of q it is possible to derive the velocities for a series of points on this catenary. In the application of this method it is by no means necessary to confine the buffer solutions to those derived from the same acid. In practice, the choice of buffer will depend on the hydrogen-ion concentration of the *M.V.* point of the water catenary, and this will vary with the nature of the catalysed reaction. When acidic or basic substances are produced in the reaction, the value of q should not be greater than, say, 10, nor less than about 0·1. Variations of q between these limits give a range of hydrogen-ion concentrations which is represented by a difference of 2·0 units on the p_H scale.

The experiments to be described have reference to the catalytic effects observed with isohydric series of buffers in the reaction between acetone and iodine. Acetate buffers were usually employed, and for these the hydrogen-ion concentration was derived from $K = 1{\cdot}85 \times 10^{-5}$. For the lowest hydrogen-ion concentration, a phosphate buffer was used, and it is necessary to consider the co-ordination of this with the acetate buffers. The measurements which permit of the derivation of a value for the second-stage dissociation constant K_2 of phosphoric acid have been recently examined by Prideaux and Ward (J., 1924, **125**, 423). It appears that the " constant " obtained for mixtures of $NaH_2PO_4 + Na_2HPO_4$ increases with the total concentration and also with the proportion of the disodium salt. The measurements which relate most nearly to the conditions in our experiments are those of Michaelis and Krüger (*Biochem. Z.*, 1921, **119**, 307), and in accordance with their results the value $1{\cdot}1 \times 10^{-7}$ has been adopted for K_2 in the derivation of the hydrogen-ion concentration.

When the observed reaction velocities for each series of isohydric solutions are plotted against the concentration of the buffer constituents, the points are found to lie very closely on straight lines as required by equations (2*a*) and (2*b*). If the extrapolated values of v_0 are then plotted against the logarithm of the hydrogen-ion concentration (see Fig. 1), a catenary curve is obtained which is symmetrical with respect to the point for which $p_H = 4{\cdot}90$, or $[H^+]_i = 1{\cdot}25 \times 10^{-5}$. This is the *M.V.* point on the water catenary, and the magnitude of the velocity v_i according to this curve (see Fig. 1) is about $0{\cdot}019 \times 10^{-6}$ mols. per litre per minute. This velocity refers to 25° and an acetone concentration of 20 c.c. per litre.

In accordance with the relations which have been shown to hold at the *M.V.* or isocatalytic point, the minimum value of the velocity due to the joint action of the hydrogen and hydroxyl ions should be given by $u_i = 2k_h[H^+]_i$. When $k_h = 4{\cdot}65 \times 10^{-4}$ and $[H^+]_i = 1{\cdot}25 \times 10^{-5}$ are substituted in this equation, we obtain $u_i = 0{\cdot}012 \times 10^{-6}$. This is clearly much lower than the minimum velocity $v_i = 0{\cdot}019 \times 10^{-6}$ which is indicated by the experiments with the buffer solutions, and it would seem fairly obvious that the difference is to be attributed to the catalytic action of undissociated water. In other words, the difference corresponds with $v_w = k_w[H_2O] = 0{\cdot}007 \times 10^{-6}$. In previous measurements of the catalytic effects which are produced by mixtures of acetic acid and sodium acetate in the series represented by $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$, the experimental data afforded no evidence of the catalytic activity of the water molecules, but the reason for this is obviously to be found in the very small magnitude of the water effect. Since the minimum velocity for the above constant-acid series is about $0{\cdot}3 \times 10^{-6}$, it is evident that the proportion of the total catalytic effect due to the water molecules is only about 2% at the *M.V.* point. For other mixtures of the series the proportion will, of course, be still smaller.

FIG. 1.



Velocity of the acetone–iodine reaction (due to the joint action of hydrogen ions, hydroxyl ions, and water molecules) plotted against p_H.

In order to compare the experimental values of v_0 with those given by equation (2), it is necessary to know the value of the coefficient k_{OH}. The difficulties associated with the determination of this have been referred to in previous papers. A preliminary estimate of $k_{OH} = 10$ was made by Dawson and Carter (*loc. cit.*) on the basis of the velocity data afforded by experiments with acid–salt mixtures belonging to the series $(0{\cdot}2 - x)CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$. Subsequently an independent value was derived from an examination of the course followed by the autocatalysed reaction between acetone and iodine (Dawson, J., 1927, 458). It was shown that the early stages of the autocatalytic change were generally consistent with the assumption that the reaction proceeds under the joint catalytic influence of the hydrogen and hydroxyl ions as represented by the equation $v = k_h[H^+] + k_{OH}[OH^-]$. The results obtained in the present investigation indicate, however, that this equation should include a term to correspond with the catalytic action of the undissociated water. For the purpose of this inquiry, it will suffice to point out that the introduction of the water term leads to a lower value for k_{OH} than that which was derived on the assumption that the water effect could be neglected, and that the present experiments seem to afford a simpler method for the determination of k_{OH}. This method is based on the equation which expresses the connexion between the hydrogen-ion concentration of the *M.V.* point on the water catenary and the catalytic coefficients k_h and k_{OH}. This equation is $[H^+]_i = \sqrt{k_{OH}K_w/k_h}$, and by substituting $[H^+]_i = 1{\cdot}25 \times 10^{-5}$, $k_h = 4{\cdot}65 \times 10^{-4}$, and $K_w = 10^{-14}$ we obtain $k_{OH} = 7{\cdot}2$. A comparison of the values of v_0 obtained from the experiments with the buffer solutions and those calculated from the equation

$$v_0 = v_h + v_{OH} + v_w = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O]$$

may now be undertaken. In Table I, the hydrogen-ion concentration is recorded in the first column; cols. 2, 3, 4, and 5 give respectively the values of v_h, v_{OH}, v_w, and v_0; and col. 6 shows the values of v_0 obtained from the buffer solution experiments.

TABLE I.

$[H^+] . 10^5$.	$v_h . 10^6$.	$v_{OH} . 10^6$.	$v_w . 10^6$.	$v_0 . 10^6$ (calc.).	$v_0 . 10^6$ (obs.).
18·5	0·086	0	0·007	0·093	0·092
5·55	0·026	0·001	0·007	0·034	0·034
1·85	0·009	0·004	0·007	0·020	0·022
0·62	0·003	0·011	0·007	0·021	0·022
0·185	0·001	0·038	0·007	0·046	0·044
0·053	0	0·126	0·007	0·133	0·135

The calculated values of v_0 are based on $k_h = 4{\cdot}65 \times 10^{-4}$, $k_{OH} = 7$, and $k_w = 0{\cdot}007 \times 10^{-6}/55 = 1{\cdot}3 \times 10^{-10}$. The ratio between the coefficients for the hydroxyl ion and the water molecule is therefore about 5×10^{10}. The close agreement between the two series of v_0 values would seem to justify the view that the procedure described affords a convenient and trustworthy method for the investigation of the relations which are involved in the joint catalytic action of the hydrogen ion, the hydroxyl ion, and the water molecule.

In so far as the reaction velocities due to the ions are concerned, it has been shown previously (Dawson, J., 1927, 213) that all the catalytic catenaries which correspond with the general formula $(H^+{-}HA{-}A^-)_c$ can be replaced by a single catenary. If the hydrogen-ion concentrations and the ionic reaction velocities are expressed in terms of the corresponding values for the respective isocatalytic or *M.V.* points, such that $n = [\mathrm{H}^+]/[\mathrm{H}^+]_i$ and $r = u/u_i$, the connexion between the reduced hydrogen-ion concentration (n) and the reduced ionic reaction velocity (r) is given by

$$r = \tfrac{1}{2}(n + 1/n) = \cosh \log_e n,$$

which is the equation of the universal catalytic catenary. By this transformation, the specific catalytic coefficients as well as the ionisation constant and concentration of the catalysing acid are eliminated.

It is of interest to examine the results obtained for the water catenary in reference to the generalised catalytic formula. Since $v_0 = 0{\cdot}019 \times 10^{-6}$ and $v_w = 0{\cdot}007 \times 10^{-6}$, the value of r is given by $u/u_i = (v_0 - v_w)/(v_0 - v_w)_i = (v_0 - 0{\cdot}007 \times 10^{-6})/0{\cdot}012 \times 10^{-6}$, and n by $[\mathrm{H}^+]/[\mathrm{H}^+]_i = [\mathrm{H}^+]/1{\cdot}25 \times 10^{-5}$. In making the comparison between the two sets of values, it should be borne in mind that the values assigned to the very small velocities v_w and u_i and also to $[\mathrm{H}^+]_i$ are necessarily only approximate. In Table II, col. 1 gives the hydrogen-ion concentration, col. 2 the reduced hydrogen-ion concentration n, col. 3 the values of $\tfrac{1}{2}(n + 1/n)$, and col. 4 the values of r.

TABLE II.

$[\mathrm{H}^+] . 10^5$.	n.	$\tfrac{1}{2}(n + 1/n)$.	r.
18·5	14·8	7·4	7·1
5·55	4·4	2·3	2·35
1·85	1·5	1·1	1·25
0·62	0·50	1·25	1·35
0·185	0·15	3·4	3·1
0·053	0·042	11·9	10·7

Having due regard for the probable degree of accuracy of the data on which the values of r and $\tfrac{1}{2}(n + 1/n)$ are based, the concordance between the two sets of figures is quite good, and it may be claimed that the results obtained in the determination of the water catenary for the acetone–iodine reaction are in agreement with the requirements of the universal catalytic relation $r = \cosh \log_e n$.

EXPERIMENTAL.

The materials used were purified by methods which have been previously described. In all cases, the concentration of the acetone was 20·0 c.c. per litre and the initial concentration of the iodine about 0·001*M*. In order to reduce the disturbing effect of the hydriodic acid, the experiments were conducted on a scale which permitted the use of 100 c.c. samples in the titration of the residual iodine with 0·01*N*-thiosulphate. The hydriodic acid produced during a reaction period which sufficed for the measurement of the velocity was about 0·0001 mol. per litre and the effect of this was eliminated by the usual method. For each value of p_H, three buffer solutions were used with relative concentrations represented by successive integers. Denoting the integral ratio by m, the velocity for each series may be expressed by $v = v_0 + am$. Such values are shown in the last column of Table III and the close agreement with the observed values in the previous column is an indication of the exactness of the linear relation.

TABLE III.

$[H^+] . 10^5$.	c.	s.	$v . 10^6$ (obs.).	$v . 10^6$ (calc.).
$CH_3{\cdot}CO_2H : CH_3{\cdot}CO_2Na = 10 : 1;\ v = 0{\cdot}092 + 0{\cdot}096m$.				
18·5	0·05	0·005	0·188	0·188
,,	0·1	0·01	0·283	0·284
,,	0·15	0·015	0·380	0·380
$CH_3{\cdot}CO_2H : CH_3{\cdot}CO_2Na = 3 : 1;\ v = 0{\cdot}034 + 0{\cdot}044m$.				
5·55	0·015	0·005	0·078	0·078
,,	0·03	0·01	0·123	0·122
,,	0·045	0·015	0·165	0·166
$CH_3{\cdot}CO_2H : CH_3{\cdot}CO_2Na = 1 : 1;\ v = 0{\cdot}022 + 0{\cdot}026m$.				
1·85	0·005	0·005	0·0485	0·048
,,	0·01	0·01	0·075	0·074
,,	0·015	0·015	0·098	0·100
,,	0·02	0·02	0·127	0·126
$CH_3{\cdot}CO_2H . CH_3{\cdot}CO_2Na = 1 : 3;\ v = 0{\cdot}022 + 0{\cdot}0625m$.				
0·62	0·005	0·015	0·0835	0·084
,,	0·01	0·03	0·148	0·147
,,	0·015	0·045	0·209	0·210
$CH_3{\cdot}CO_2H : CH_3{\cdot}CO_2Na = 1 : 10;\ v = 0{\cdot}044 + 0{\cdot}192m$.				
0·185	0·005	0·05	0·236	0·236
,,	0·01	0·10	0·430	0·428
,,	0·015	0·15	0·610	0·620
$NaH_2PO_4 : Na_2HPO_4 = 4{\cdot}80 : 1;\ v = 0{\cdot}135 + 0{\cdot}685m$.				
0·065	$c + s = 0{\cdot}01$		0·82	0·82
,,	,, $= 0{\cdot}02$		1·50	1·50
,,	,, $= 0{\cdot}03$		2·20	2·19

The velocities for the phosphate buffer indicate that catalytic effects of considerable magnitude are brought about by the buffer constituents.

Summary.

Measurements of the rate of the reaction between acetone and iodine in isohydric series of buffer solutions have been used to derive the velocities which are due to the catalytic constituents of water as represented by $v_0 = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O]$.

The reaction is accelerated by water molecules, although the coefficient k_w is very small. The ratio of k_{OH} to k_w is about 5×10^{10}.

The velocity due to the joint action of the hydrogen and hydroxyl ions is found to be in agreement with the requirements of the generalised catalytic formula $r = \cosh \log_e n$, in which r is the reduced ionic velocity and n the reduced hydrogen-ion concentration.

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