CCLXXXI.—*Acid and Salt Effects in Catalysed Reactions. Part XXIV. A Study of the Catalytic Effects produced by Acetic Acid and Acetate Buffers under Conditions of Effectively Constant Ionic Environment.*

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PREVIOUS kinetic measurements relating to the catalytic influence of acetic acid and of acetate buffers on the acetone-iodine reaction have led to the conclusion that the observed reaction velocity corresponds with the sum of a series of catalytic effects represented by the equation

$$v = k_h[\mathrm{H}^{\cdot}] + k_a[\mathrm{A}'] + k_m[\mathrm{HA}] + k_{\mathrm{OH}}[\mathrm{OH}'] + k_w[\mathrm{H_2O}] \quad (1)$$

In the calculation of the velocities from this equation it was assumed that the ionisation constant of the acetic acid and the catalytic coefficients of the several catalytically active entities are not affected by the varying ionic concentration of the solutions. Although this assumption, which was definitely provisional and preliminary in character, cannot be justified as the basis of a general method of procedure, it is nevertheless a fact that the relations between the primary and the secondary catalytic effects are in this case such as to warrant with a close degree of approximation the procedure which was actually followed in the interpretation of the earlier results (compare Dawson and Carter, J., 1926, 2282).

In more recent work attention has been given to the secondary (indirect) effects which are attributable to variations in the reaction medium, and more particularly to those which are caused by changes in the electrolyte content of the solutions. The results obtained permit us to define the conditions under which the comparative study of catalytic effects may be carried out with a minimum of disturbance from variations in the electrical environment of the reactants, and the present paper gives an account of such observations.

The changes which take place in the ionisation coefficient $K = [\mathrm{H}^{\bullet}][\mathrm{A}']/[\mathrm{HA}]$ of a weak acid on the addition of chemically inert salts can be expressed by the equation $\log K = \log K_0 + a\sqrt{x} - bx$, in which x is the concentration of the added uni-univalent salt and K_0 is the limiting value of K when $x = 0$. According to this equation, the form of which it may be noted is consistent with the Debye–Hückel theory, the value of K passes through a maximum when $x = a^2/4b^2$. In the neighbourhood of this value of x, variations in the electrolyte content of the solution have but little influence on the magnitude of K and in accordance with the results obtained by Dawson and Key (J., 1928, 1239) and by Dawson and Lowson (J., 1929, 1217), which indicate that the maximum value of K in solutions of sodium chloride corresponds approximately with $x = 0{\cdot}75$, the experiments to be described have been carried out in a 0·75 molar solution of sodium chloride.

With regard to the dependence of the catalytic coefficients on the salt content of the solution, it is well known that the coefficient k_h usually increases on the addition of inert salts, but the magnitude of this effect varies considerably with the nature of the salt, and its influence cannot be determined for salts which are catalytically active. Much less is known about the influence of inert salts on the catalytic coefficients which characterise the acid anion and the undissociated acid, but these would appear to be much less susceptible than the hydrogen-ion coefficient to changes in the reaction medium.

Under these circumstances it cannot be asserted that constancy of the catalytic coefficients is definitely assured by the use of $0{\cdot}75N$-sodium chloride as the reaction medium, but, on the other hand, it may be noted that the catalytic effect of the hydrogen ion is reduced to such an extent by the addition of quite small quantities of sodium acetate that variations in the magnitude of k_h are not of importance. It might be suggested that more constant conditions would be obtained by the use of solutions in which the total salt concentration (chloride + acetate) has a fixed value, but in the absence of knowledge of the inert-salt effects which are attributable to sodium acetate, it is not actually possible to say that greater uniformity of environment would be obtained under such circumstances.

In so far as the experimental data can be represented by equation (1), it will suffice to refer to previous papers for the derivation of the various theoretical relations which follow from this equation. The more extensive study of the catalytic effects which is afforded by the present series shows, however, the necessity for the addition of a further term to equation (1). In this connexion, attention may be directed to the buffer mixtures of the series $c\ CH_3{\cdot}CO_2H + s\ CH_3{\cdot}CO_2Na$ (c constant, s variable), for which the plot of the reaction velocity against the salt concentration shows that the velocity falls rapidly to a minimum and then increases linearly with the salt concentration. In the original experiments of Dawson and Carter (*loc. cit.*) the slope of this line was found to be approximately the same for $c = 0{\cdot}1$ and $c = 0{\cdot}2$, and in accordance with equation (1) the mean value of the slope dv/ds was interpreted as a measure of the catalytic coefficient for the acetate ion (k_a). With the larger variation of c in the present experiments, it is established, however, that the slope of the linear portion of the v–s curve depends on the acid concentration, and is indeed a linear function of c. This result may be explained if the acetate buffers are assumed to contain the complex acetate ion HA_2' formed by combination of the simple ion with the undissociated acid. The relation between the concentrations of these entities is given by $K' = [HA_2']/[A'][HA]$, where K' is the complex constant, and if the concentration of the complex ion is small in comparison with that of the simple ion and of the undissociated acid, it follows that the concentration of the complex ion is given approximately by $[HA_2'] = K'cs$. The catalytic coefficient for the complex anion being denoted by k_a', equation (1) becomes

$$\begin{aligned} v &= v_h + v_a + v'_a + v_m + v_{OH} + v_w \\ &= k_h[H^{\cdot}] + k_a[A'] + k_a'[HA_2'] + k_m[HA] + k_{OH}[OH'] + k_w[H_2O] \quad (2) \end{aligned}$$

In the application of this equation to the acetate buffers which correspond with the approximately linear portions of the v–s curves, it may be noted that the catalytic effects represented by v_h, v_{OH}, and v_w form but a very small proportion of the total effect if c is not less than $0{\cdot}1$. If $v_h + v_{OH} + v_w = v_0$, then $v' = v - v_0$ represents the sum of the effects due to the simple and the complex anions and the undissociated acid, and we obtain for this range of buffers

$$v' = k_a s + k_a'K'c\,.\,s + k_m c \quad . \quad . \quad . \quad . \quad (2a)$$

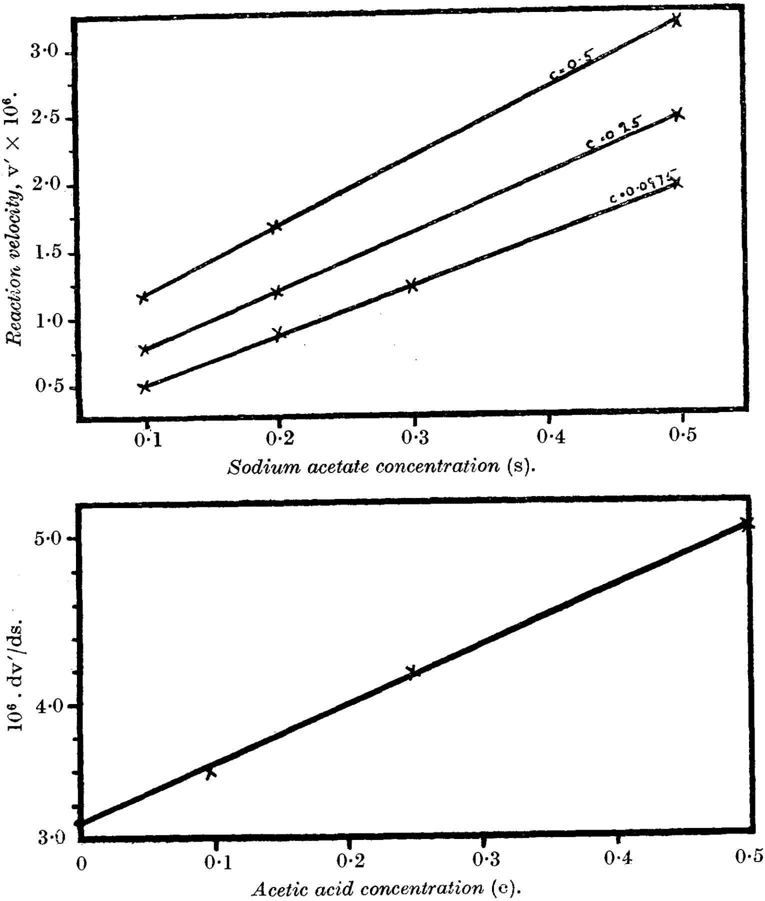
from which, if c is constant,

$$dv'/ds = k_a + k_a'K'c \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and if s is constant,

$$dv'/dc = k_m + k_a'K's \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

FIG. 1.



The upper section shows the plot of the reaction velocity v′ *against the salt concentration* s, *for three series of buffer mixtures in which the concentration of the acetic acid is respectively* 0·0975, 0·25, *and* 0·5 *mol. per litre. The lower section shows that the slope of these plots is a linear function of the acetic acid concentration* c *as required by equation* (3).

The linear portions of the v'–s curves for three constant-acid series of buffers are shown in Fig. 1. The values of dv'/ds corresponding with these are $3{\cdot}60 \times 10^{-6}$ for $c = 0{\cdot}0975$, $4{\cdot}20 \times 10^{-6}$ for $c = 0{\cdot}25$, and $5{\cdot}05 \times 10^{-6}$ for $c = 0{\cdot}5$ respectively. When these values of dv'/ds are plotted against c (Fig. 1, lower section) a straight line is obtained which cuts the ordinate for $c = 0$ at about $3{\cdot}3 \times 10^{-6}$, and this, according to equation (3), represents the value of k_a. The slope of this line gives $ka'K' = 3{\cdot}5 \times 10^{-6}$. In the same way the data for constant-acetate series of buffers with $s = 0{\cdot}1$, $s = 0{\cdot}2$, and $s = 0{\cdot}5$ lead to values of $dv'/dc = 1{\cdot}60$, $2{\cdot}05$, and $3{\cdot}0 \times 10^{-6}$, respectively. The plot of these against s gives a straight line which cuts the ordinate $s = 0$ at about $1{\cdot}30 \times 10^{-6}$, which, according to equation (4), represents the value of k_m. The slope of this line gives $k_a'K' = 3{\cdot}4 \times 10^{-6}$, in close agreement with the value afforded by the data for the constant-acid buffers.

The catalytic data do not permit us to resolve the quantity $k_a'K'$ into its components, and so long as the magnitude of the complex anion constant K' is unknown it is not possible to assign a value to the catalytic coefficient k_a'. The product $k_a'K'$ is actually a measure of the catalytic effect of the complex anion in a solution which is normal with respect to both the undissociated acid and the simple acetate ion.

In connexion with the above interpretation it may be recalled that acetic acid is considerably polymerised both in the vapour state and when dissolved in solvents of low dielectric capacity such as benzene, chloroform, etc., whereas freezing-point data for aqueous solutions show that the un-ionised acid consists almost entirely of simple molecules. With reference to the nature of the negative ions, little information is to be derived from the conductivity, although, according to Davies (*Phil. Mag.*, 1927, **4**, 244), the conductance relations even in dilute solution are not quite normal. Apart from measurements of the variation of the hydrogen electrode potential, the physico-chemical properties of acetate buffers have not been systematically examined. In such solutions the effect of complex ion formation should be most apparent, and it is significant that acid acetates have been crystallised from concentrated acid–salt mixtures (Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114). The changes produced in the partial vapour pressure of acetic acid solutions on the addition of salts (McBain and Kam, J., 1919, **115**, 1332) show that the effect of sodium acetate is very small in comparison with that of sodium chloride. This may be mainly due to the difference in salting-out capacity, but the fixation of acetic acid by complex anion formation is by no means to be excluded as a contributory factor. In a general way the facts above-mentioned may be said to lend support to the views which seem to be suggested by the catalytic behaviour of acetate buffers.

According to the nature of the series of solutions examined, the experiments to be described fall into four groups—(*a*) constant-acid buffers, (*b*) pure acetic acid, (*c*) acetic acid + hydrochloric acid, (*d*) isohydric buffers. In the calculation of the reaction velocities from equation (2) the values of the catalytic coefficients used are $k_h = 561 \times 10^{-6}$, $k_a = 3{\cdot}35 \times 10^{-6}$, $k_m = 1{\cdot}30 \times 10^{-6}$, $k_a'K' = 3{\cdot}5 \times 10^{-6}$, $k_{OH} = 7$, and $v_w = k_w[H_2O] = 0{\cdot}006 \times 10^{-6}$, all of which refer to an acetone concentration of 20·0 c.c. per litre and 25°. The value of k_h is based on measurements with 0·01*N*-hydrochloric acid as catalyst and those for k_{OH} and v_w on the data for isohydric buffers, which will be discussed in due course. At this point it is sufficient to note that the catalytic effect represented by v_{OH} is in general very small and that an accurate knowledge of k_{OH} is not of essential importance. The value $K = 2{\cdot}6 \times 10^{-5}$ which has been used for the ionisation coefficient of acetic acid is derived from the data relating to the ionisation of acetic acid in sodium chloride solutions (compare Dawson and Key, J., 1928, 1248; Dawson and Lowson, *loc. cit.*). For $K_w = [H^{\cdot}][OH']$ the value $1{\cdot}2 \times 10^{-14}$ has been used.

Catalytic Activity of Constant-acid Buffers.—The results for buffers of the type c $CH_3{\cdot}CO_2H$ + s $CH_3{\cdot}CO_2Na$ with constant c and variable s are shown in detail in Table I. Column 1 gives the value of s; column 2 the hydrogen-ion concentration derived from $[H^{\cdot}] = K(c - [H^{\cdot}])/(s + [H^{\cdot}])$; columns 3 to 8 the partial velocities due respectively to hydrogen ion (v_h), acetate ion (v_a), complex acetate ion (v_a'), undissociated acetic acid (v_m), hydroxyl ion (v_{OH}), and undissociated water (v_w); column 9 the total calculated velocity ($v_{cal.}$) and column 10 the observed velocity ($v_{obs.}$). In this and the following tables the velocities are expressed in terms of 10^{-6} mol. per litre per minute.

The partial velocities recorded in the table show clearly the large variations in the relative importance of the several catalytic entities. For the most part, the agreement between the calculated and the observed velocities is very close, and the important part which may be played by the complex ion is evident from the figures for the most concentrated series of solutions.

Catalytic Activity of Acetic Acid.—In acetate-free solutions of acetic acid, the hydrogen ion and the undissociated acid are almost entirely responsible for the observed catalytic effects. In considering the results it may be noted that the presence of complex anions would tend to increase the concentration of the hydrogen ion, the effect becoming more marked as the concentration of the solution increases. This follows from the equation for electroneutrality $[H^{\cdot}] = [A'] + [HA_2']$ and the equilibrium expressions

TABLE I.

s.	$[\mathrm{H}^{\cdot}]\,.\,10^4$.	v_h.	v_a.	$v_a{}'$.	v_m.	v_{OH}.	v_w.	$v_{\mathrm{cal.}}$.	$v_{\mathrm{obs.}}$.
$0{\cdot}5\mathrm{CH_3{\cdot}CO_2H} + s\text{-}\mathrm{CH_3{\cdot}CO_2Na}$.									
0	35·9	2·015	0·012	—	0·645	—	0·006	2·68	2·69
0·01	11·60	0·652	0·037	0·018	0·649	—	0·006	1·36	1·39
0·02	6·30	0·353	0·079	0·035	0·65	—	0·006	1·12	1·16
0·04	3·22	0·170	0·135	0·070	0·65	—	0·006	1·03	1·05
0·08	1·62	0·091	0·260	0·140	0·65	—	0·006	1·15	1·18
0·1	1·30	0·073	0·335	0·175	0·65	—	0·006	1·24	1·23
0·2	0·65	0·036	0·670	0·350	0·65	—	0·006	1·71	1·72
0·5	0·26	0·014	1·675	0·875	0·65	—	0·006	3·22	3·19
$0{\cdot}25\mathrm{CH_3{\cdot}CO_2H} + s\text{-}\mathrm{CH_3{\cdot}CO_2Na}$.									
0·1	0·65	0·037	0·335	0·088	0·325	0·002	0·006	0·795	0·81
0·2	0·325	0·018	0·670	0·175	0·325	0·003	0·006	1·20	1·22
0·5	0·13	0·007	1·675	0·438	0·325	0·008	0·006	2·46	2·48
$0{\cdot}0975\mathrm{CH_3{\cdot}CO_2H} + s\text{-}\mathrm{CH_3{\cdot}CO_2Na}$.									
0	15·8	0·885	0·005	—	0·125	—	0·006	1·02	1·015
0·01	2·47	0·138	0·034	0·004	0·127	—	0·006	0·309	0·315
0·02	1·26	0·071	0·067	0·007	0·127	0·001	0·006	0·279	0·285
0·05	0·51	0·028	0·168	0·018	0·127	0·002	0·006	0·349	0·349
0·1	0·26	0·014	0·335	0·034	0·127	0·004	0·006	0·520	0·523
0·2	0·13	0·007	0·670	0·068	0·127	0·008	0·006	0·885	0·895
0·3	0·09	0·005	1·005	0·103	0·127	0·012	0·006	1·26	1·25
0·5	0·05	0·003	1·675	0·172	0·127	0·020	0·006	2·00	1·98
$0{\cdot}0195\mathrm{CH_3{\cdot}CO_2H} + s\text{-}\mathrm{CH_3{\cdot}CO_2Na}$.									
0	6·99	0·392	0·002	—	0·024	—	0·006	0·424	0·425
0·004	1·22	0·069	0·014	—	0·025	0·001	0·006	0·115	0·120
0·008	0·62	0·035	0·027	0·001	0·025	0·002	0·006	0·096	0·102
0·01	0·50	0·028	0·034	0·001	0·025	0·002	0·006	0·096	0·102
0·02	0·25	0·014	0·067	0·002	0·025	0·004	0·006	0·118	0·124
0·04	0·13	0·007	0·134	0·003	0·025	0·008	0·006	0·183	0·182
0·06	0·09	0·005	0·201	0·004	0·025	0·012	0·006	0·253	0·252
0·10	0·05	0·003	0·335	0·007	0·025	0·020	0·006	0·398	0·395
0·16	0·03	0·002	0·536	0·011	0·025	0·032	0·006	0·612	0·605

$K = [\mathrm{H}^{\cdot}]\,.\,[\mathrm{A}']/[\mathrm{HA}]$ and $K' = [\mathrm{HA}_2']/[\mathrm{A}'][\mathrm{HA}]$, for it may be readily shown that the combination of these leads to

$$[\mathrm{H}^{\cdot}] = \sqrt{K[\mathrm{HA}] + KK'[\mathrm{HA}]^2}$$

or approximately $[\mathrm{H}^{\cdot}] = \sqrt{Kc(1 + K'c)}$.

Since the value of K' is not known, the influence of complex ion formation on the hydrogen-ion concentration cannot be determined and indeed it seems possible that the effect in question may be more than counterbalanced by the reduced ionising capacity of the medium at the higher acetic acid concentrations. In this connexion it may be recalled that the value of K which is derived from conductivity data falls from $1{\cdot}85 \times 10^{-5}$ for dilute solutions to $1{\cdot}40 \times 10^{-5}$ in a molar solution. Under these circumstances the calculated reaction velocities recorded in Table II are those derived on the assumption that the effect of complex ion formation can be neglected in pure acetic acid solutions.

TABLE II.

Catalytic Activity of Acetic Acid.

c	0·0195	0·0975	0·195	0·390	0·5	0·75	1·0
$v_{obs.}$	0·425	1·015	1·50	2·33	2·69	3·48	4·18
$v_{cal.}$	0·424	1·02	1·52	2·30	2·68	3·46	4·17

The close agreement between the observed and the calculated velocities suggests that any measurable effect of complex ion formation in the most concentrated solutions is neutralised by the reduced ionising capacity of the reaction medium.

Catalytic Activity of Acetic–Hydrochloric Acid Mixtures.—It may be anticipated that the ionisation of acetic acid will be equally affected by the addition of equivalent quantities of hydrochloric acid or of sodium acetate. In the presence of the strong acid the acetate ion is buffered in the same way that the hydrogen ion is buffered in the presence of an acetate. In spite of the stoicheiometric parallelism, two such series of solutions differ completely in their catalytic relations, but this divergence is, of course, entirely due to the difference in the order of magnitude of k_h and of k_a. It is for this reason that the observations in this series are of necessity confined to solutions in which the hydrochloric acid concentration is small. The concentrations of the catalytically active entities in the solution $c\ CH_3{\cdot}CO_2H + x\ HCl$ are given by

$$[H^{\cdot}] = \sqrt{K(c + x) - \left(\frac{x - K}{2}\right)^2} + \frac{x - K}{2}, \quad [A'] = [H^{\cdot}] - x,$$

and $[HA] = c + x - [H^{\cdot}]$ and having regard to the fact that complex ion formation must be less important in these solutions than in solutions of pure acetic acid, it follows that equation (2) reduces to the form $v = v_h + v_a + v_m + v_w$. The calculated and the observed reaction velocities are compared in Table III and show close agreement.

TABLE III.

Catalytic Activity of $0{\cdot}0975CH_3{\cdot}CO_2H + xHCl$.

x	0	0·002	0·004	0·008	0·01
$v_{obs.}$	1·015	1·76	2·71	4·75	5·78
$v_{cal.}$	1·02	1·75	2·74	4·74	5·89

Catalytic Activity of Isohydric Buffers.—The results previously obtained in pure aqueous solution with buffer mixtures characterised by a constant ratio of acetic acid to acetate (Dawson and Hoskins, *Proc. Leeds Phil. Soc.*, 1926, **1**, 108) showed that the reaction velocity is a linear function of the buffer concentration when this is not very large. On the assumption that the linear relation is valid down to zero buffer concentration, the data for such mixtures were used for the purpose of determining by extrapolation the values of $v_0 = v_h + v_{\mathrm{OH}} + v_w$ for the hydrogen-ion concentrations peculiar to each of a series of such isohydric buffers. Since the ionisation constant of the acid is, however, particularly susceptible to the influence of the ionic environment at low salt concentrations, it has been deemed advisable to carry out corresponding experiments in 0·75M-sodium chloride solution. In view of the small concentrations of the buffer mixtures, the secondary effects arising from variations in the ionic environment may be said to be completely eliminated.

The results for five isohydric series in which the ratio c/s varies from 3·0 to 0·125 show that in each case the reaction velocity increases linearly with the buffer concentration. The data recorded in Table IV show the acid/salt ratio in column 1; the values of $[\mathrm{H}^{\cdot}]$, c, and s in columns 2, 3, and 4; the observed reaction velocity in column 5, the velocity calculated from equation (2) in column 6, and the value of $v_0 = v_h + v_{\mathrm{OH}} + v_w$, derived by linear extrapolation of the observed velocities, in column 7.

TABLE IV.

Catalytic Activity of Isohydric Buffers.

Acid/salt.	$[\mathrm{H}^{\cdot}] . 10^5$.	c.	s.	$v_{\mathrm{obs.}}$.	$v_{\mathrm{cal.}}$.	v_0.
3 : 1	7·80	0·01	0·0033	0·083	0·081	
,,	,,	0·025	0·0083	0·123	0·118	0·056
,,	,,	0·05	0·167	0·187	0·180	
1 : 1	2·60	0·01	0·01	0·075	0·072	
,,	,,	0·02	0·02	0·125	0·119	0·0255
,,	,,	0·04	0·04	0·222	0·217	
1 : 2	1·30	0·008	0·016	0·085	0·087	
,,	,,	0·01	0·02	0·102	0·104	0·023
,,	,,	0·02	0·04	0·183	0·186	
,,	,,	0·04	0·08	0·366	0·354	
1 : 3	0·87	0·005	0·015	0·078	0·081	
,,	,,	0·01	0·03	0·139	0·139	0·025
,,	,,	0·02	0·06	0·249	0·256	
,,	,,	0·04	0·12	0·476	0·496	
1 : 8	0·32	0·005	0·04	0·185	0·188	
,,	,,	0·01	0·08	0·325	0·330	0·047
,,	,,	0·014	0·112	0·435	0·446	
,,	,,	0·02	0·16	0·605	0·630	

Throughout the above table there is again close agreement between the observed and the calculated velocities and, as required, the value of $v_0 = v_h + v_{\mathrm{OH}} + v_w$ passes through a minimum. The minimum is attained when $k_h[\mathrm{H}^{\cdot}] = k_{\mathrm{OH}}[\mathrm{OH}']$ and, since $[\mathrm{H}^{\cdot}][\mathrm{OH}'] = K_w$, it follows that this condition corresponds with the hydrogen-ion concentration $[\mathrm{H}^{\cdot}]_i = \sqrt{k_{\mathrm{OH}}K_w/k_h}$ and with the velocity represented by $2k_h[\mathrm{H}^{\cdot}]_i + v_w$. By plotting v_0 against $\log[\mathrm{H}^{\cdot}]$ it is found that the minimum occurs at $\log[\mathrm{H}^{\cdot}] = \bar{5}\cdot16$ or $[\mathrm{H}^{\cdot}]_i = 1\cdot45 \times 10^{-5}$ and that the actual minimum velocity is $0{\cdot}0223 \times 10^{-6}$. Since $2k_h[\mathrm{H}^{\bullet}]_i = 0{\cdot}0163$, it follows that $v_w = 0{\cdot}006 \times 10^{-6}$. This value of v_w is within the limits of error identical with that derived by Dawson and Key (J., 1928, 543) from observations on similar series of isohydric buffers in pure aqueous solution. The results obtained in sodium chloride solution thus confirm the conclusion that a small but measurable catalytic effect is to be attributed to the water molecule.

In the previous experiments with solutions containing equivalent quantities of acetic acid and sodium acetate (Dawson and Hoskins, *loc. cit.*) the velocity obtained for the mixture $N\text{-}CH_3{\cdot}CO_2H + N\text{-}CH_3{\cdot}CO_2Na$ was $8{\cdot}05 \times 10^{-6}$. This large value could not be accounted for in terms of the acetate ion and the acetic acid molecule, and the formation of a catalytically effective complex ion was suggested. In further support of this hypothesis it may be stated that the velocity calculated from equation (2), using the coefficients recorded in this paper, is $8{\cdot}15 \times 10^{-6}$.

Apart from the fact that the present experiments suggest an addition to the list of catalytic agents which are associated with acetate buffers, the relations disclosed by observations under conditions which afford approximate constancy of the ionic environment are thus exactly of the same kind as those indicated by the earlier experiments in which the reactants were dissolved in pure water.

Summary.

The catalytic effects associated with the acetone–iodine reaction in the presence of acetic acid and acetate buffers have been studied in 0·75*N*-sodium chloride solution which provides for approximate constancy of the ionic environment.

The results confirm those previously obtained with pure water as the solvent medium.

In the case of acetate buffers for which the catalytic effects produced by the hydrogen ion, the hydroxyl ion, and the water molecule are very small, the observations suggest that a further catalytic agent is involved, and this has been identified with the complex acetate ion $CH_3{\cdot}CO_2H,CH_3{\cdot}CO_2'$.

The equation $v = k_h[\mathrm{H}^{\bullet}] + k_a[\mathrm{A}'] + k_a'[\mathrm{HA}_2'] + k_m[\mathrm{HA}] + k_{\mathrm{OH}}[\mathrm{OH}'] + k_w[\mathrm{H_2O}]$ affords a complete and satisfactory account of the observations.

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