

XIII.—*Acid and Salt Effects in Catalysed Reactions.*
 Part XXIII. *The Catalytic Activity of Acid Salts with Reference to the Catalytic Effects produced by Potassium Hydrogen Oxalate in the Acetone-Iodine Reaction.*

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IN two previous papers (Dawson, Hoskins, and Smith, J., 1929, 1884; Dawson and Smith, *ibid.*, p. 2530) an account has been given of the catalytic effects associated with oxalic acid in the first and second stages of ionisation. The experimental work relates to the effects produced by mixtures of acid and salt represented respectively by $c\text{H}_2\text{C}_2\text{O}_4 + x\text{KHC}_2\text{O}_4$ and $c\text{KHC}_2\text{O}_4 + x\text{K}_2\text{C}_2\text{O}_4$, where c is constant and x is variable, and further, to the influence of inert salts on the primary and secondary ionisation of oxalic acid. The relations disclosed by these observations permit us to proceed to the detailed consideration of the catalytic properties of solutions of the binoxalate.

The interesting problem presented by the catalytic activity of the acid salts of polybasic acids does not appear to have been subjected to systematic investigation, and the results of the present enquiry indicate that their behaviour cannot be explained in terms of any form of the simple hydrogen-ion theory.

The hydrogen-ion concentration of solutions of an acid salt of the type MHA is given by

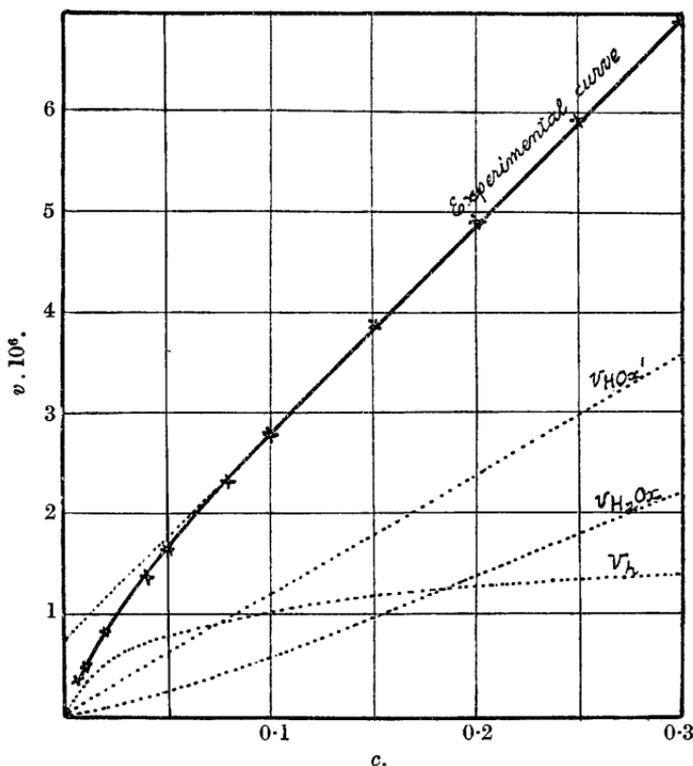
$$[\text{H}^+] = \sqrt{K_1 K_2 [\text{HA}'] / (K_1 + [\text{HA}'])}$$

where K_1 and K_2 are the mass-law constants for the first and second stages of dissociation of the acid H_2A . This reduces to $[\text{H}^+] = \sqrt{K_1 K_2}$ if the concentration (c) of the acid salt is large compared with K_1 , and to $[\text{H}^+] = \sqrt{K_2(c - [\text{H}^])}$ if c is small in comparison with K_1 . If K_2 is small the latter expression becomes $[\text{H}^+] = \sqrt{K_2 c}$. In so far as the hydrogen ion is responsible for the catalytic effects in the

solutions of an acid salt, it may therefore be anticipated that the connexion between the reaction velocity and the concentration of the acid salt will depend on the relative magnitudes of c and K_1 .

The restricted solubility of the binoxalates imposes a rather low upper limit to the range of concentration of the solutions which may be used for the study of the catalytic effects. In pure aqueous solution, the range extends from about $c = 0.01$ to $c = 0.3$ mol. per

FIG. 1.



Plot of reaction velocity against concentration. The full curve represents the experimental data and shows the deviations from linearity at low concentrations. The dotted curves show the variation of the partial velocities v_h , v_{H_2Ox} , and v_{HOx} .

litre, and since the mean value of K_1 for this series of solutions may be taken as 0.08, it follows that c is less than K_1 for the less concentrated, and greater than K_1 for the more concentrated solutions of the series. This circumstance has a direct bearing on the relations which are shown by the measured reaction velocities.

The observations were made at 25° with an acetone concentration of 20.0 c.c. per litre, and the usual procedure was followed in determining the initial velocity. By plotting this against the concen-

tration, it is found (see Fig. 1) that the velocity varies almost linearly with the concentration when $c > 0.1$, but that at lower concentrations dv/dc increases as c diminishes.

In accordance with previous results, the specific reaction velocity may be represented by the equation

$$v = k_h[H^*] + k_{H_2Ox}[H_2Ox] + k_{HOx'}[HOx'] + k_{Ox''}[Ox''] \quad (1)$$

in which the concentrations of the various catalytic entities are given by

$$[H^*] = \sqrt{K_1 K_2 [HOx'] / (K_1 + [HOx'])}, [H_2Ox] = [H^*][HOx'] / K_1, \\ [HOx'] = c - [H^*] - 2[H_2Ox], \text{ and } [Ox''] = [H^*] + [H_2Ox].$$

The magnitude of the ionisation constants and of the catalytic coefficients varies with the nature and concentration of the ionic environment and such variations must be taken into account as far as possible in the application of equation (1).

Since the binoxalate ion is neither catalytically nor chemically inert, it is not possible to determine the inert-salt effects peculiar to an atmosphere of potassium and binoxalate ions by the methods which are permissible in the case of solutions of salts which are both chemically and catalytically inert. In these circumstances it has been assumed that the values of K_1 and K_2 for the binoxalate solutions are the same as for the corresponding solutions of potassium chloride. For the latter it has been shown (*loc. cit.*) by experiments relating to the first and second stages of ionisation that the values are given by

$$\log K_1 = \bar{2}.756 + 0.42\sqrt{x} - 0.275x$$

and

$$\log K_2 = \bar{5}.857 + 0.81\sqrt{x} - 0.39x,$$

in which x , the total salt concentration, corresponds in the present paper with the molar concentration (c) of the binoxalate.

With regard to the variations in the catalytic coefficients, it may be recalled that the available evidence would seem to show that the hydrogen ion is considerably more susceptible than other catalytic entities to changes in environment. The effects in question are specific in the sense that they depend on the nature of the ions in the solution, and as already pointed out, they cannot be determined for a solution of potassium binoxalate. Since, however, the maximum salt concentration in our experiments is only 0.3 mol. per litre, it is permissible as a first approximation to assume that k_h is not affected by the presence of the binoxalate. In support of this procedure, it may be noted that the catalytic effect due to the hydrogen ion in the more concentrated solutions is only a small fraction of the total effect. The reaction velocities recorded in

Table I are therefore based on the following values for the various catalytic coefficients, *viz.*, $k_h = 465 \times 10^{-6}$, $k_{H_2Ox} = 210 \times 10^{-6}$, $k_{HOx'} = 13.0 \times 10^{-6}$, and $k_{Ox''} = 1 \times 10^{-6}$. The first column gives the concentration of the binoxalate; the second, third, fourth, and fifth give the partial velocities due to the hydrogen ion, the undissociated oxalic acid, the binoxalate ion, and the oxalate ion respectively; the sixth shows the calculated, and the seventh the observed velocity.

TABLE I.

Catalytic activity of aqueous solutions of potassium hydrogen oxalate.

<i>c.</i>	$v_h \cdot 10^6.$	$v_{H_2Ox} \cdot 10^6.$	$v_{HOx'} \cdot 10^6.$	$v_{Ox''} \cdot 10^6.$	$v \cdot 10^6.$ (calc.).	$v \cdot 10^6.$ (obs.).
0.005	0.270	0.009	0.056	—	0.335	0.315
0.01	0.382	0.025	0.111	0.001	0.52	0.49
0.02	0.535	0.069	0.235	0.001	0.84	0.82
0.04	0.72	0.175	0.480	0.002	1.37	1.37
0.05	0.79	0.24	0.60	0.003	1.63	1.62
0.08	0.94	0.44	0.96	0.004	2.34	2.32
0.10	1.02	0.58	1.20	0.005	2.80	2.79
0.15	1.16	0.97	1.79	0.007	3.93	3.88
0.20	1.27	1.37	2.39	0.009	5.04	4.91
0.25	1.36	1.79	2.99	0.011	6.15	5.90
0.30	1.43	2.22	3.59	0.014	7.25	6.90

The autocatalytic effect of the hydriodic acid produced in the reaction sets a lower limit to the concentration of the binoxalate solutions for which the reaction velocity can be measured with accuracy. Within the available range of concentrations it is clear from the table that equation (1) affords a satisfactory account of the measured velocities. The systematic divergence at the higher concentrations suggests that the increase in K_1 and K_2 may not be so great for the binoxalate as for the corresponding chloride.

By plotting the partial velocities against the concentration of the acid salt, it is found that $v_{HOx'}$ is a linear function of c , and v_{H_2Ox} very nearly so when c is greater than 0.1, whilst v_h tends towards a maximum value. These relations are consistent with the fact that the experimental v - c curve is approximately linear for $c > 0.1$. The slope of this linear portion of the curve corresponds with $dv/dc = 20 \times 10^{-6}$, and when extrapolated to $c = 0$, the line in question is found to cut the zero ordinate at about $v = 0.8 \times 10^{-6}$, which, it may be noted, is nearly three times as great as the velocity at the smallest concentration. In connexion with this very considerable initial velocity which seems to be indicated by the linear portion of the experimental v - c curve, it may be recalled that the hydrogen-ion concentration approximates to the value $[H^+] = \sqrt{K_1 K_2}$ when c becomes large in comparison with K_1 . If this value of $[H^+]$ is

combined with the stoichiometric equation $c = [\text{H}_2\text{Ox}] + [\text{HOx}'] + [\text{Ox}']$ and the mass-action expressions

$$K_1 = [\text{H}^+][\text{HOx}']/[\text{H}_2\text{Ox}] \text{ and } K_2 = [\text{H}^+][\text{Ox}']/[\text{HOx}']$$

we obtain

$$[\text{H}_2\text{Ox}] = c[\text{H}^+]^2/([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) = c\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2})$$

$$[\text{HOx}'] = cK_1[\text{H}^+]/([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) = c\sqrt{K_1}/(\sqrt{K_1} + 2\sqrt{K_2})$$

and

$$[\text{Ox}'] = cK_1K_2/([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) = c\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2})$$

Putting $\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2}) = \gamma$ and $\sqrt{K_1}/(\sqrt{K_1} + 2\sqrt{K_2}) = \delta$, and substituting the values of $[\text{H}^+]$, $[\text{H}_2\text{Ox}]$, $[\text{HOx}']$, and $[\text{Ox}']$ in equation (1), the latter becomes

$$v = k_h\sqrt{K_1K_2} + \{(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'} \cdot \delta\}c \quad (2)$$

according to which, apart from variations in K_1 and K_2 , the v - c curve should be a straight line the slope of which is given by the value of $(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'} \cdot \delta$. Since γ and δ are not greatly affected by the variations in K_1 and K_2 , the slope may be determined with some precision. If, for instance, we utilise the values of K_1 and K_2 which correspond with $c = 0.2$, namely, $K_1 = 7.8 \times 10^{-2}$ and $K_2 = 14 \times 10^{-5}$, then $\gamma = 0.039$ and $\delta = 0.93$, and for $(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'}\delta$ we obtain 20.3×10^{-6} , which agrees closely with the slope of the linear portion of the experimental curve.

The term $k_h\sqrt{K_1K_2}$ in the above velocity equation obviously corresponds with the initial velocity which is indicated when the approximately linear v - c curve is extrapolated to $c = 0$. This curve is actually slightly concave to the c axis, which means that the slope of the tangent decreases and therefore that the intercept on the zero concentration ordinate increases as the value of c increases. This may be due in part to the circumstance that the hydrogen-ion concentration has not reached the value represented by $\sqrt{K_1K_2}$ within the range of the concentrations actually used, but it is also quite probably attributable in part to the increase in K_1 and K_2 which occurs when the concentration increases. In any case, the velocity measurements are not accurate enough to permit of the determination of the variation of the intercept with the concentration of the binoxalate, and it must suffice to record the fact that linear extrapolation of the velocities for the higher concentrations leads to a velocity for $c = 0$ which corresponds fairly closely with the magnitude $k_h\sqrt{K_1K_2}$.

To provide further support for the conclusions suggested by the data recorded in Table I, a parallel series of measurements has been made with solutions in which the ionic strength was kept constant at $\mu = 0.3$ by the addition of potassium chloride. This series is represented by $c\text{KHC}_2\text{O}_4 + (0.3 - c)\text{KCl}$. In the application of equation (1) to these solutions, the constant values taken for K_1 and K_2 are those corresponding with $0.3M$ -potassium chloride, and the value of k_h is assumed to be determined by the potassium chloride content of the solutions. The arrangement of Table II, in which the results are recorded, is exactly similar to Table I.

TABLE II.

Catalytic activity of potassium hydrogen oxalate in solutions of constant ionic strength ($\mu = 0.3$).

c .	$v_h \cdot 10^6$.	$v_{\text{H}_2\text{Ox}} \cdot 10^6$.	$v_{\text{HOx}'} \cdot 10^6$.	$v_{\text{Ox}''} \cdot 10^6$.	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).
0.02	0.74	0.07	0.23	0.002	1.04	1.09
0.04	0.965	0.185	0.47	0.003	1.62	1.67
0.08	1.19	0.46	0.95	0.005	2.60	2.59
0.10	1.24	0.60	1.19	0.005	3.04	3.05
0.15	1.34	0.99	1.79	0.008	4.13	4.08
0.20	1.39	1.39	2.39	0.010	5.18	4.99
0.25	1.42	1.80	2.98	0.012	6.21	5.94
0.30	1.43	2.22	3.59	0.014	7.25	6.90

The v - c curve corresponding to the second series of observations is of the same general character as the curve for the chloride-free solutions and need not be discussed in detail. There is, of course, no suggestion that constancy of ionic strength affords conditions of ionic environment which entitle the results in Table II to be regarded as strictly comparable. The combined results for the two series afford, however, considerable justification for the belief that inert-salt effects, in so far as they have not been allowed for, are of very minor significance, and that equation (1) provides a satisfactory basis for the interpretation of the experimental data.

Both sets of observations show that the connexion between the reaction velocity and the concentration of the acid salt varies with the latter. The connexion is approximately linear for the more concentrated solutions of the series. The hydrogen-ion concentration of these solutions varies within very narrow limits and the observed catalytic effects are mainly due to the binoxalate ion and the undissociated oxalic acid, the concentrations of which vary linearly with the total concentration of the acid salt. In the more dilute solutions, on the other hand, the dominant catalyst is the hydrogen ion, and as the concentration falls there is a gradual

approach to a condition in which the reaction velocity is essentially determined by the hydrogen-ion concentration.

The results show conclusively that the catalytic activity of acid salts is in large measure due to the catalytic action of the acid ion (HA') and of the undissociated acid (H_2A).

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