CCXLVI.—*Acid and Salt Effects in Catalysed Reactions. Part XXI. The Catalytic Effects associated with Oxalic Acid in the First and Second Stages of Dissociation.*

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The systematic study of the catalytic effects which are associated with a partially ionised acid HA is facilitated by the use of mixtures of the acid with the corresponding salt, for these afford a convenient means of adjusting the relative magnitudes of the concentrations of the hydrogen ion, acid anion, and undissociated acid so as to permit of the investigation of the corresponding individual catalytic activities. Since the ionisation constant of the acid and the catalytic coefficients vary with the salt content of the solutions, the interpretation of the experimental data which are obtained by the use of such buffer mixtures should also take account of the inert-salt effects which depend on the ionic concentration of the solvent medium.

In accordance with recent observations (Dawson and Lowson, this vol., p. 1217) it would appear that the changes produced in the ionisation constant of an acid by the addition of an inert salt can be represented by the equation

$$\log K_x/K_0 = a\sqrt{x} - bx,$$

in which K_0 is the ionisation constant of the acid in salt-free solution and K_x that in a solution containing x mols. of salt per litre. The coefficient a would seem to be nearly independent of the nature of the (univalent) ions, but larger variations are shown by b when the nature of the ions changes.

The similarity of the above equation to that which follows from the interionic attraction theory has already been discussed (*loc. cit.*), and it will suffice here to recall that the coefficient a is much smaller than the corresponding coefficient which follows from the Debye–Hückel theory.

From the equation connecting K_x and x, it is apparent that the ionisation constant of the acid changes rapidly with the salt concentration when the latter is small. With increase of x it reaches a maximum and then decreases. The maximum increase observed with uni-univalent salts of the alkali metals is about 75%.

With regard to the variations of the catalytic coefficients, this is not of much importance so long as we are concerned with salt solutions of moderate concentration. The available evidence is confined almost entirely to the hydrogen ion, and in this case the variation of the catalytic coefficient is found to depend on the nature of the inert salt.

At the outset, it may also be pointed out that the study of inert-salt effects is necessarily restricted to salts of the monobasic acids. This limitation is due to the circumstance that the constants which characterise the second and subsequent stages of the dissociation of polybasic acids are not large enough to permit of the realisation of that condition of inertness which is attained when, for example, sodium chloride is added to the solution of an acid. Such a solution affords no evidence of the formation of hydrochloric acid in catalytically effective quantity, and the catalytic activity of the sodium and chlorine ions is also negligibly small. On the other hand, if the sodium chloride is replaced by the salt of a dibasic acid, *e.g.*, sodium sulphate, then since the constant K_2 for the second-stage dissociation of sulphuric acid is relatively small, interaction will take place between the hydrogen and sulphate ions with the formation of the highly active complex anion HSO_4'. Apart from this, it may not be justifiable to neglect the effect which is produced by the relatively weak bivalent anion SO_4''. For these reasons, it is in general not possible to give any simple interpretation to observations on salt effects when the salts of polybasic acids come into question.

Whilst the importance of the inert-salt effect under certain conditions may be admitted, the experimental evidence which has been referred to above shows that it is not possible to make allowance for such effects by the introduction of general correction factors based on the concept of ionic strength and the Debye–Hückel interionic attraction constant. Within the limits which are imposed by the specificity of the inert-salt effects, consideration has been given to the latter in the interpretation of the observations described in the present paper. In following this procedure, it should nevertheless be emphasised that the observations can be interpreted in their essential features and with a fair degree of exactitude without taking into account the variable inert-salt effects. The agreement between the observed and calculated results is, however, definitely improved when the appropriate salt-effect corrections are introduced.

The investigation of the catalytic behaviour of oxalic acid arose from a desire to compare the catalytic effects which are associated with the stages of dissociation represented by $H_2C_2O_4 \rightleftharpoons H^{\cdot} + HC_2O_4'$ and $HC_2O_4' \rightleftharpoons H^{\cdot} + C_2O_4''$. According to Drucker (*Z. physikal. Chem.*, 1920, **96**, 381), the values of K_1 and K_2 derived from the analysis of *E.M.F.*, freezing-point, and conductivity data are $K_1 = 5{\cdot}7 \times 10^{-2}$ and $K_2 = 6{\cdot}9 \times 10^{-5}$. These numbers are, of course, based on the interpretation of the data in accordance with the classical ionic theory. On account of the large difference between the two constants, the overlap between the successive stages of dissociation is relatively small, and for this reason the study of the catalytic effects is to some extent simplified. On the other hand, the fact that acid oxalates of various types separate from acidified oxalate solutions suggests that oxalate ions other than HC_2O_4' and C_2O_4'' may be present in such solutions. In particular, the stability of the ion $(HC_2O_4,H_2C_2O_4)'$ may have some connexion with the fact that quadroxalates of the type $MH_3(C_2O_4)_2,2H_2O$ are deposited from all solutions of the alkali-metal oxalates which contain oxalic acid in excess of the ratio $H_2C_2O_4 : M_2C_2O_4 = 1 : 1$ (Foote and Andrew, *Amer. Chem. J.*, 1905, **34**, 153). There is, however, no quantitative evidence for the existence of this ion in solution, and it has therefore been assumed that the only anionic constituents are HC_2O_4' and C_2O_4''.

The experimental work refers to the catalysis of the acetone–iodine reaction at 25° with an acetone concentration of 20 c.c. per litre. In the case of the larger velocities, this was reduced to 8·0 c.c. per litre but the recorded data relate uniformly to the 20 c.c. basis. The oxalic acid was purified by repeated crystallisation. The observations relating to the two stages of dissociation are separately considered.

Catalytic Behaviour of Oxalic Acid in the First Stage of Dissociation.

In the first stage, the effective catalysts involved are the hydrogen ion, the oxalic acid molecule, and the anion HC_2O_4'. Their combined action is represented by

$$v = v_h + v_{\mathrm{HOx}'} + v_{\mathrm{H_2Ox}} = k_h[\mathrm{H}^\bullet] + k_{\mathrm{HOx}'}[\mathrm{HOx}'] + k_{\mathrm{H_2Ox}}[\mathrm{H_2Ox}] \quad (1)$$

From the magnitude of the ionisation constant K, it was to be expected that the coefficient $k_{\mathrm{H_2Ox}}$ would be about 200×10^{-6}. In view of the dual part played by HOx′ in the two stages of the oxalic acid dissociation, it did not seem possible, however, to predict with certainty the magnitude of the coefficient $k_{\mathrm{HOx}'}$. The procedure followed in determining its value will be described in connexion with the observations on the second stage. This method gives $k_{\mathrm{HOx}'} = 13 \times 10^{-6}$, and by combination with $K_1 = 5{\cdot}7 \times 10^{-2}$, this may be used for the calculation of $k_{\mathrm{H_2Ox}}$ from the experimental data for salt-free solutions of oxalic acid (compare Table I). For this purpose equation (1) may be written

$$k_{\mathrm{H_2Ox}} = \{v - (k_h + k_{\mathrm{HOx}'})[\mathrm{H}^\bullet]\}/(c - [\mathrm{H}^\bullet]) \quad . \quad . \quad (2)$$

and by substitution of the values of v and $[\mathrm{H}^\bullet]$ for the more concentrated solutions, in which the catalytic effect of the undissociated oxalic acid is relatively more important, the value obtained for $k_{\mathrm{H_2Ox}}$ is 210×10^{-6}.

An alternative method of procedure, which, moreover, does not require a knowledge of the ionisation constant K_1, is afforded by the relation

$$k_{\mathrm{H_2Ox}} = (v_i/\sqrt{c} - v_i'/\sqrt{c'})/(\sqrt{c} - \sqrt{c'})$$

in which v_i is the minimum reaction velocity for the series of acid–salt mixtures $c\mathrm{H_2C_2O_4} + x\mathrm{KHC_2O_4}$, and v_i' is the corresponding velocity for the series in which the concentration of the oxalic acid is c'. The experimental data for $c = 0{\cdot}05$ and $c' = 0{\cdot}02$ give for the minimum velocities $16{\cdot}40 \times 10^{-6}$ and $7{\cdot}80 \times 10^{-6}$ respectively, and substitution of these leads to $k_{\mathrm{H_2Ox}} = 220 \times 10^{-6}$. It may be recalled that the above formula (Dawson and Hoskins, J., 1926, 3166) involves the assumption that the ionisation constant and the catalytic coefficients are not affected by the salt which is present in the solutions for which the reaction velocity is a minimum. It may be shown that the value of $k_{\mathrm{H_2Ox}}$ obtained by the minimum-velocity method is for this reason probably about 5% greater than the true value, and $k_{\mathrm{H_2Ox}} = 210 \times 10^{-6}$ has therefore been adopted.

Having thus obtained values which measure the specific activities of the various catalytic entities, the experimental results may be examined. Table I records the data for pure oxalic acid solutions; the concentration of the acid is given in the first column and the observed velocity in the last. The hydrogen-ion concentration is shown in the second, the partial velocities in the third, fourth, and fifth, and the total calculated velocity in the sixth; these numbers are derived from $K_1 = 5{\cdot}7 \times 10^{-2}$, $k_h = 465 \times 10^{-6}$, $k_{\mathrm{HOx'}} = 13{\cdot}0 \times 10^{-6}$, and $k_{\mathrm{H_2Ox}} = 210 \times 10^{-6}$. The agreement between the observed and calculated reaction velocities is remarkably good, and it should be noted that the latter have been derived on the basis of a fixed value for K_1. The relations which are hereby shown by the pure oxalic acid solutions are quite similar to those which have been previously observed with various other acids (compare Dawson, Hall, and Key, J., 1928, 2844), and suggest that the interionic force effect in such solutions is relatively very small.

TABLE I.

Reaction velocities for oxalic acid solutions.

c.	[H·].	$v_h \cdot 10^6$.	$v_a \cdot 10^6$.	$v_m \cdot 10^6$.	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).
0·01	0·00867	3·83	0·11	0·28	4·22	4·35
0·025	0·0188	8·74	0·25	1·30	10·3	10·20
0·05	0·0320	14·9	0·42	3·78	19·1	19·2
0·10	0·0522	24·3	0·67	10·05	35·0	35·6
0·20	0·0820	38·1	1·06	24·8	64·0	64·6
0·25	0·0943	43·8	1·22	32·7	77·7	77·6
0·3	0·1055	49·1	1·37	40·8	91·3	91·6
0·4	0·1252	58·2	1·63	57·8	117·6	116·0
0·5	0·1427	66·3	1·86	75·0	143·2	143·8

When the experimental data for acid–salt mixtures of the type $c\mathrm{H_2C_2O_4} + x\mathrm{KHC_2O_4}$ are analysed in the same way, differences between the observed and calculated velocities are found which indicate that the ionisation constant K_1 increases with the salt concentration. Supplementary measurements have therefore been made with mixtures represented by $0{\cdot}05\mathrm{H_2C_2O_4} + x\mathrm{KCl}$ in order to ascertain to what extent the ionisation constant of the acid may be affected by inert-salt action. From the reaction-velocity data for this series, the ionisation constants have been derived by the method described in the preceding paper (Dawson and Lowson, *loc. cit.*). The results are summarised in Table II, which shows the concentration (x) of the potassium chloride, the value of k_h derived from experiments with $0{\cdot}01\text{HCl} + x\text{KCl}$, the observed reaction velocity v_x, and the ionisation constant K_x which follows from the experimental data.

TABLE II.

Ionisation of oxalic acid in potassium chloride solutions.

x	0·04	0·06	0·10	0·40	0·50	1·0	2·0	3·0
$k_h . 10^6$	470	472	477	512	523	582	699	830
$v_x . 10^6$	19·6	19·8	20·1	21·5	21·9	23·7	26·8	29·8
$K_x . 10^2$	6·6	7·0	7·5	8·2	8·2	7·5	6·0	4·8
$K_x . 10^2$ (calc.)	6·7	6·9	7·3	8·1	8·2	7·9	6·3	4·6

On account of the large extent to which the oxalic acid is ionised, the accuracy of the individual values of K_x is rather limited, but it is evident that the relations are quite similar to those which have been disclosed by the investigation of other acids in solutions of inert salts. The observed connexion between $R_x = K_x/K_0$ and x can be expressed by $\log R_x = 0{\cdot}42\sqrt{x} - 0{\cdot}275x$, and from the values of R_x given by this equation, the numbers recorded in the last row of the table have been calculated from $K_x = K_0R_x = 0{\cdot}057R_x$.

In applying the results afforded by the potassium chloride experiments to the interpretation of the data for mixtures of oxalic acid and potassium hydrogen oxalate, it must be assumed that this salt and the chloride have the same influence on the ionisation constant K_1. This may not be entirely justifiable but there is no alternative. The observed and calculated velocities for two series of acid–salt mixtures of the type $c\text{H}_2\text{C}_2\text{O}_4 + x\text{KHC}_2\text{O}_4$ are shown in Table III. The second column shows the ionisation constant

TABLE III.

x.	K_1.	[H·].	$v_h . 10^6$.	$v_a . 10^6$.	$v_m . 10^6$.	$v . 10^6$ (calc.).	$v . 10^6$ (obs.).
			$0{\cdot}05\text{H}_2\text{C}_2\text{O}_4 + x\text{KHC}_2\text{O}_4$.				
0	0·057	0·0320	14·88	0·41	3·78	19·1	19·2
0·02	0·064	0·0285	13·25	0·64	4·51	18·4	18·6
0·04	0·067	0·0253	11·76	0·85	5·19	17·8	18·0
0·08	0·071	0·0207	9·62	1·31	6·15	17·1	17·0
0·10	0·073	0·0189	8·79	1·55	6·53	16·85	16·6
0·14	0·075	0·0162	7·53	2·03	7·10	16·65	16·4
0·16	0·076	0·0151	7·02	2·27	7·33	16·6	16·4
0·20	0·078	0·0134	6·23	2·77	7·68	16·7	16·6
			$0{\cdot}02\text{H}_2\text{C}_2\text{O}_4 + x\text{KHC}_2\text{O}_4$.				
0	0·057	0·0157	7·30	0·20	0·90	8·40	8·45
0·015	0·063	0·0137	6·37	0·37	1·32	8·05	8·1
0·03	0·066	0·0122	5·67	0·54	1·64	7·85	7·9
0·05	0·069	0·0106	4·93	0·78	1·97	7·70	7·8
0·09	0·072	0·0084	3·90	1·27	2·43	7·60	7·8
0·10	0·073	0·0080	3·75	1·40	2·52	7·65	7·85
0·12	0·074	0·0072	3·35	1·65	2·69	7·70	8·0
0·15	0·076	0·0065	3·05	2·03	2·83	7·90	8·2

for each salt concentration, but apart from this the headings of the columns are the same as those in Table I.

In spite of the limited solubility of the potassium hydrogen oxalate, it has been possible in both the above series to increase the value of x until the minimum velocity indicated by theory is attained. Throughout both series the agreement between the observed and calculated velocities is good. The difference between the catalytic effect of the free acid and that of the minimum-velocity mixture is quite small—about 15% in the first series and less in the second. This is due, on the one hand, to the high catalytic activity of the undissociated oxalic acid, and on the other, to the abnormally large value of the coefficient $k_{HOx'}$ in comparison with the value for the anion of a monobasic acid of similar strength. This point will be referred to later.

Catalytic Behaviour of Oxalic Acid in the Second Stage of Dissociation.

In passing from the first to the second stage, the oxalic acid molecule is replaced by the binoxalate ion HC_2O_4', and the place of the latter is taken by the bivalent ion C_2O_4''. The principal difference in the catalytic effects which are associated with the two stages is intimately connected with the difference in the magnitude of the ionisation constants K_1 and K_2.

So far as the second stage is concerned, the experimental data have reference to acid–salt mixtures of the constant acid type represented by $c\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$. The reaction-velocity measurements for such solutions are complicated to some extent by the oxidising action of iodine on the oxalate (C_2O_4'') ion. According to Dhar (J., 1917, **111**, 713; 1923, **123**, 1856) and Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307) this is a photochemically accelerated reaction, the velocity of which is greatly reduced in the absence of light. This observation has been confirmed, and to minimise the effect of this disturbing factor, the reaction-velocity measurements were made in the dark, blank experiments with acetone-free solutions being carried out in order to provide the necessary corrections. Such experiments show that the velocity is very nearly proportional to the concentration of the added neutral oxalate and may be derived from the equation $v = 0{\cdot}65 \times 10^{-6}x$.

In view of the small magnitude of K_2, the hydrogen-ion concentration of a binoxalate solution may be reduced to a value at which the catalytic effect of the hydrogen ion is relatively unimportant by the addition of small quantities of the normal oxalate. When this stage is reached, changes in the ionisation constant due to the increase in the salt concentration can be almost ignored. In this respect the conditions approximate to the simple state of affairs which is met with in the case of acetate buffers.

When the observed velocities for the series $c\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$ are corrected for the reaction between the iodine and the oxalate ion, a v–x curve is obtained which shows a rapid initial fall followed by a slow linear increase in the reaction velocity. If the very small effects due to the hydrogen ion are ignored, the linear portion of the curve is represented by $v = c \, . \, k_{\mathrm{HOx'}} + x \, . \, k_{\mathrm{Ox''}}$, and it follows that $k_{\mathrm{HOx'}}$ may be derived by extrapolation to $x = 0$, and $k_{\mathrm{Ox''}}$ from the slope of this line. The values so obtained from the experiments with $0{\cdot}1\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$ are $k_{\mathrm{HOx'}} = 13 \times 10^{-6}$ and $k_{\mathrm{Ox''}} = 1{\cdot}0 \times 10^{-6}$. In so far as this method of procedure has been criticised on the ground that salt effects are not specifically taken into consideration (Brönsted, *Trans. Faraday Soc.*, 1928, **24**, 630; Wynne-Jones, *ibid.*, p. 725; Harned and Åkerlöf, *ibid.*, p. 666; Soper and Pryde, J., 1927, 2761), we would point out that this is due to a misconception of the actual importance of such salt effects under the conditions afforded by the experiments in question.

Before the coefficients $k_{\mathrm{HOx'}}$ and $k_{\mathrm{Ox''}}$ can be utilised for the calculation of reaction velocities for mixtures of binoxalate and oxalate, it is necessary to examine more closely the constitution of such solutions, for it appears that in spite of the large difference between K_1 and K_2, such mixtures may contain undissociated oxalic acid in quantities which, on account of the large value of $k_{\mathrm{H_2Ox}}$, give rise to a very appreciable catalytic effect. The relations between the concentrations of the catalytically active entities in the solution $c\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$ may be derived from the following equations.

Since the total concentration of the oxalate radical is $c + x$ we have

$$[\mathrm{HOx'}] + [\mathrm{Ox''}] + [\mathrm{H_2Ox}] = c + x \quad . \quad . \quad . \quad (3)$$

and in accordance with the electro-neutrality of the solutions

$$[\mathrm{HOx'}] + 2[\mathrm{Ox''}] = [\mathrm{K}^{\cdot}] + [\mathrm{H}^{\cdot}] = c + 2x + [\mathrm{H}^{\cdot}] \quad . \quad . \quad (4)$$

Combination of these equations leads to

$$[\mathrm{H}^{\cdot}] = [\mathrm{Ox''}] - [\mathrm{H_2Ox}] - x \quad . \quad . \quad . \quad . \quad (5)$$

and the mass-law expressions for K_1 and K_2 give

$$[\mathrm{H}^{\cdot}][\mathrm{HOx'}]/[\mathrm{H_2Ox}] = K_1 \quad . \quad . \quad . \quad . \quad (6)$$

$$[\mathrm{H}^{\cdot}][\mathrm{Ox''}]/[\mathrm{HOx'}] = K \quad . \quad . \quad . \quad . \quad (7)$$

Since the hydrogen ion and the undissociated acid are much more active as catalysts than the binoxalate and oxalate ions, the primary object to be attained in the consideration of these equations is the determination of $[\mathrm{H}^{\bullet}]$ and $[\mathrm{H_2Ox}]$. The required values of $[\mathrm{H}^{\bullet}]$ and $[\mathrm{H_2Ox}]$ may be derived from equations (5), (6), and (7), which lead to

$$[\mathrm{H}^{\bullet}] = \sqrt{\frac{K_1}{K_1 + [\mathrm{HOx}']}K_2[\mathrm{HOx}'] + \left(\frac{K_1}{K_1 + [\mathrm{HOx}']}\cdot\frac{x}{2}\right)^2} - \frac{K_1}{K_1 + [\mathrm{HOx}']}\cdot\frac{x}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$[\mathrm{H_2Ox}] = [\mathrm{H}^{\bullet}][\mathrm{HOx}']/K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

from which, if x is not too small, these relatively small quantities may be derived with sufficient accuracy by substituting $[\mathrm{HOx}'] = c$. The concentration of the oxalate ion is then obtained from equation (5), which may be written

$$[\mathrm{Ox}''] = [\mathrm{H}^{\bullet}] + [\mathrm{H_2Ox}] + x \quad . \quad . \quad . \quad . \quad (10)$$

and the concentration of the binoxalate ion by combining equations (3) and (5), whereby we obtain

$$[\mathrm{HOx}'] = c - [\mathrm{H}^{\bullet}] - 2[\mathrm{H_2Ox}] \quad . \quad . \quad . \quad (11)$$

If necessary, the value of $[\mathrm{HOx}']$ given by equation (11) may be substituted in equations (8) and (9) for the derivation of more accurate values of $[\mathrm{H}^{\bullet}]$ and $[\mathrm{H_2Ox}]$. In this way the concentrations of the various catalytic entities may be derived if K_1, K_2, c, and x are known. The values of the two ionisation constants depend, however, on the concentration of the salt solutions, and to some extent on the nature of the constituent ions. In the case of K_1, the variation has been studied by experiments with oxalic acid dissolved in potassium chloride solutions (see Table II), and similar experiments with potassium hydrogen oxalate, which will be described in a later paper, provide information in regard to the variation of K_2. Since the concentrations of the hydrogen ion and of the undissociated oxalic acid diminish rapidly with increase of x, no attempt has been made to take account of the variations of K_1 and K_2 with increasing quantities of oxalate, and, moreover, the values actually used are those indicated by the observations made with solutions of potassium chloride.

In order to illustrate the procedure followed in the calculation of the reaction velocities, the solution $0{\cdot}1\mathrm{KHC_2O_4} + 0{\cdot}02\mathrm{K_2C_2O_4}$ may be considered in detail. By adoption of the values $K_1 = 0{\cdot}073$ (corresponding to $0{\cdot}1N$-saline solution, see Table II) and $K_2 = 1{\cdot}1 \times 10^{-4}$, equations (8) to (11) give $[\mathrm{H}^{\bullet}] = 0{\cdot}00052$, $[\mathrm{H_2Ox}] =$

0·00071, [HOx′] = 0·098, and [Ox″] = 0·021. The corresponding partial reaction velocities are

$$\begin{aligned}
v_h &= k_h[\mathrm{H}^{\cdot}] &&= 465 \times 10^{-6} \times 0{\cdot}00052 &&= 0{\cdot}24 \times 10^{-6} \\
v_{\mathrm{H_2Ox}} &= k_{\mathrm{H_2Ox}}[\mathrm{H_2Ox}] &&= 210 \times 10^{-6} \times 0{\cdot}00071 &&= 0{\cdot}15 \times 10^{-6} \\
v_{\mathrm{HOx'}} &= k_{\mathrm{HOx'}}[\mathrm{HOx'}] &&= 13{\cdot}0 \times 10^{-6} \times 0{\cdot}098 &&= 1{\cdot}27 \times 10^{-6} \\
v_{\mathrm{Ox''}} &= k_{\mathrm{Ox''}}[\mathrm{Ox''}] &&= 1{\cdot}0 \times 10^{-6} \times 0{\cdot}02 &&= 0{\cdot}02 \times 10^{-6}
\end{aligned}$$

and the total reaction velocity $v = 1{\cdot}68 \times 10^{-6}$.

The velocities recorded in Table IV have been derived in this manner. In the case of the pure binoxalate solution ($x = 0$) there is, however, an appreciable difference between c and [HOx′], and the preliminary value of [HOx′] obtained by the above procedure has been substituted for c in equations (8) and (9) in order to obtain more accurate values of [H˙] and [H_2Ox]. The partial velocities due to the hydrogen ion, the undissociated oxalic acid, the binoxalate ion, and the oxalate ion are shown in cols. 2—5, the calculated total velocity in col. 6 and the observed velocity in col. 7.

TABLE IV.

$0{\cdot}1\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$; $K_1 = 0{\cdot}073$; $K_2 = 1{\cdot}1 \times 10^{-4}$.

x.	$v_h \,.\, 10^6$.	$v_{\mathrm{H_2Ox}} \,.\, 10^6$.	$v_{\mathrm{HOx'}} \,.\, 10^6$.	$v_{\mathrm{Ox''}} \,.\, 10^6$.	$v \,.\, 10^6$ (calc.).	$v \,.\, 10^6$ (obs.).
0	0·99	0·56	1·20	0·005	2·75	2·80
0·02	0·24	0·15	1·27	0·02	1·68	1·67
0·025	0·195	0·12	1·275	0·025	1·61	1·61
0·04	0·115	0·07	1·29	0·04	1·52	1·52
0·1	0·05	0·03	1·30	0·10	1·48	1·45
0·2	0·025	0·015	1·30	0·20	1·54	1·57
0·3	0·015	0·01	1·30	0·30	1·62	1·66
0·4	0·01	0·01	1·30	0·40	1·72	1·78

$0{\cdot}05\mathrm{KHC_2O_4} + x\mathrm{K_2C_2O_4}$; $K_1 = 0{\cdot}068$; $K_2 = 1{\cdot}0 \times 10^{-4}$.

x.	$v_h \,.\, 10^6$.	$v_{\mathrm{H_2Ox}} \,.\, 10^6$.	$v_{\mathrm{HOx'}} \,.\, 10^6$.	$v_{\mathrm{Ox''}} \,.\, 10^6$.	$v \,.\, 10^6$ (calc.).	$v \,.\, 10^6$ (obs.).
0	0·77	0·23	0·60	0·003	1·60	1·60
0·005	0·37	0·12	0·625	0·005	1·12	1·06
0·015	0·15	0·05	0·64	0·015	0·85	0·87
0·025	0·095	0·03	0·65	0·025	0·80	0·78
0·035	0·07	0·02	0·65	0·035	0·77	0·76
0·055	0·045	0·015	0·65	0·055	0·76	0·775
0·075	0·035	0·01	0·65	0·075	0·77	0·79
0·10	0·03	0·01	0·65	0·10	0·79	0·82

From the above table it is apparent that the catalytic properties of mixtures of the acid and normal oxalates can be satisfactorily accounted for in terms of the catalytic coefficients which have been assigned to the hydrogen, binoxalate, and oxalate ions when due regard is paid to the catalytic effect of the undissociated oxalic acid which is present in such buffer solutions. It may be pointed out that closer agreement would be obtained if the value of $k_{\mathrm{Ox''}}$ were raised from $1{\cdot}0 \times 10^{-6}$ to $1{\cdot}2 \times 10^{-6}$. The accuracy with which this small coefficient can be determined is, however, strictly limited, and an error of 20% is not impossible.

The Catalytic Coefficients k_{H_2Ox} *and* $k_{HOx'}$.—According to Brönsted (*loc. cit.*), the connexion between the catalytic activity of an acid and its ionisation constant can be represented by an equation of the form $k_m = aK^n$, in which the exponent n is positive and less than unity. By reference to the data for the acetone–iodine reaction with acid catalysts ranging in strength from propionic to dichloroacetic, it has been shown (Dawson and Lowson, *loc. cit.*) that the connexion between the catalytic activity of the undissociated acid and the ionisation constant can be represented very closely by the equation $k_m/k_h = 3{\cdot}0K^{0{\cdot}34}$. When this empirical relation is applied to oxalic acid with $K_1 = 0{\cdot}057$, the value obtained for k_{H_2Ox} is 220×10^{-6}, which is only about 5% greater than the value 210×10^{-6} derived from the reaction-velocity data for oxalic acid solutions of varying concentration (compare Table I).

With regard to the catalytic activity of HC_2O_4', the observed coefficient is very much greater than would be expected from the results obtained for the anions of moderately strong monobasic acids. In the case of dichloroacetic acid ($K = 5 \times 10^{-2}$), the acetone–iodine experiments afford no evidence of any measurable catalytic effect which can be attributed to the anion. On the other hand, when the coefficient $k_{HOx'}$ is compared with those for the undissociated molecules of monobasic acids with ionisation constants in the neighbourhood of K_2 for oxalic acid, it is found that the catalytic coefficients are of the same order of magnitude. It follows that the HC_2O_4' ion behaves catalytically as an acid: its rôle is that of a proton donator as opposed to a proton acceptor. At the same time, it should be noted that the value $k_{HOx'} = 3{\cdot}0 \times 10^{-6}$, which is derived from the empirical relation $k_m = 3{\cdot}0k_h \,.\, K^{0{\cdot}34}$ by the use of Drucker's value $K_2 = 6{\cdot}9 \times 10^{-5}$, is considerably smaller than the observed value. It may be that this divergence is due to the circumstance that electrically charged acids of the type represented by the binoxalate ion are not directly comparable with electrically neutral acids in so far as their catalytic activity is related to the corresponding ionisation constant. The systematic investigation of the behaviour of such complex anions may throw some light on the question.

The results of this investigation of the catalytic effects produced by oxalic acid in its two dissociation stages are in complete agreement with the general relations which have been established by recent work on acid and salt effects in catalysed reactions.

Summary.

The catalytic effects produced by oxalic acid in the first and second stages of dissociation have been studied in experiments with the acetone–iodine reaction.

The values derived for the catalytic coefficients are: Undissociated oxalic acid, $k_{H_2Ox} = 210 \times 10^{-6}$; binoxalate ion ($HC_2O_4'$), $k_{HOx'} = 13 \times 10^{-6}$; oxalate ion ($C_2O_4''$), $k_{Ox''} = 1{\cdot}0 \times 10^{-6}$, as compared with $k_h = 465 \times 10^{-6}$ for the hydrogen ion.

Inert-salt effects have been examined by experiments with oxalic acid in potassium chloride solutions; the variation of the ionisation constant with the salt concentration is similar to that observed with other acids.

Although buffer mixtures of the type $cH_2C_2O_4 + xKHC_2O_4$ afford evidence of changes in the ionisation constant of the acid with the salt concentration, the behaviour of free oxalic acid solutions suggests that interionic forces are of little importance in salt-free solutions. This is in agreement with observations made with solutions of other acids.

The magnitude of the coefficient $k_{HOx'}$ indicates that the catalytic action of the binoxalate ion is determined by its tendency to produce hydrogen ions by dissociation and not by the opposite tendency to form electrically neutral molecules by combination with hydrogen ions.

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