388. *Catalytic Effects produced by Tartaric Acid, Sodium Hydrogen Tartrate, and by First- and Second-stage Tartrate Buffers.*

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PREVIOUS investigations of the nature of the catalytic effects produced by acids and their buffer mixtures include a detailed study of the behaviour of oxalic acid in the first and second stages of dissociation (Dawson, Hoskins, and Smith, J., 1929, 1884; Dawson and Smith, J., 1929, 2530; 1930, 79). The constants for the two stages of dissociation of oxalic acid are widely separated ($K_1 = 5.7 \times 10^{-2}$, $K_2 = 7.2 \times 10^{-5}$, $K_1/K_2 = ca.$ 800) and this simplifies to some extent the interpretation of the observed catalytic effects.

The present paper gives an account of the behaviour of tartaric acid and its salts. For this acid, the two stages of dissociation are much less widely separated, in that the ratio K_1/K_2 is probably less than 30. This difference is reflected in the general character of the kinetic data for the two acids and their buffer mixtures. With oxalic acid, the constants K_1 and K_2 can both be readily obtained from measurements of the velocity of the acetone–iodine reaction. Similar observations lead without any difficulty to a value of K_1 for tartaric acid, but on account of the overlap in the two stages of dissociation, it is only possible to derive an approximate value for K_2.

The systematic investigation of the effects produced in this reaction at 25° by tartaric acid, sodium hydrogen tartrate, and by first- and second-stage buffer mixtures shows quite definitely that catalytic activity must be attributed to the tartaric acid molecule, the bitartrate ion, and the bivalent tartrate ion, and that conditions

may be readily obtained in which the effects produced by other catalytically active entities are relatively unimportant.

For the evaluation of the several catalytic coefficients and the quantitative interpretation of the measured reaction velocities, it is necessary to know the concentrations of the various catalysts, and the procedure followed in this connexion may be illustrated by reference to the first-stage buffer mixtures represented by the general formula $c\mathrm{H_2T} + x\mathrm{NaHT}$.

For such solutions, stoicheiometric and electro-neutrality considerations lead to

$$[\mathrm{H_2T}] + [\mathrm{HT'}] + [\mathrm{T''}] = c + x \quad . \quad . \quad . \quad (1)$$

$$[\mathrm{HT'}] + 2[\mathrm{T''}] = x + [\mathrm{H^{\cdot}}] \quad . \quad . \quad . \quad . \quad (2)$$

whilst the mass-law relations give

$$[\mathrm{H^{\cdot}}][\mathrm{HT'}]/[\mathrm{H_2T}] = K_1 \ (3); \ \ [\mathrm{H^{\cdot}}][\mathrm{T''}]/[\mathrm{HT'}] = K_2 \quad . \quad (4)$$

These lead to

$$[\mathrm{H^{\cdot}}] = K_1(c - [\mathrm{H^{\cdot}}] + [\mathrm{T''}])/(x + [\mathrm{H^{\cdot}}] - 2[\mathrm{T''}]) \quad . \quad (5)$$

and

$$[\mathrm{T''}] = K_2(x + [\mathrm{H^{\cdot}}] - 2[\mathrm{T''}])/[\mathrm{H^{\cdot}}] \quad . \quad . \quad . \quad (6)$$

An approximate value of $[\mathrm{H^{\cdot}}]$ is first obtained from (3), and this when substituted in (6) gives an approximate value of $[\mathrm{T''}]$ which is then introduced into (5) to obtain a more nearly correct value of $[\mathrm{H^{\cdot}}]$, the process being repeated if necessary. The values of $[\mathrm{H_2T}]$ and $[\mathrm{HT'}]$ are then given by

$$[\mathrm{H_2T}] = c - [\mathrm{H^{\cdot}}] + [\mathrm{T''}] \quad . \quad . \quad . \quad . \quad (7)$$

$$[\mathrm{HT'}] = x + [\mathrm{H^{\cdot}}] - 2[\mathrm{T''}] \quad . \quad . \quad . \quad . \quad (8)$$

In determining the constitution of solutions of tartaric acid, sodium hydrogen tartrate and second-stage buffer mixtures, similar equations are applicable, and the procedure followed is essentially the same.

It is well known that the mass-action coefficients K_1 and K_2 vary with the salt content of the solution, and this influence of environment on the value of K_1 for tartaric acid has been examined in detail with results which are exactly similar to those previously found in the investigation of the behaviour of monobasic acids (Dawson and Lowson, J., 1929, 1217). By the substitution of an inert-salt solution for water as the solvent medium, it would be possible to reduce very considerably the variations of K_1 and K_2, but, on the other hand, it is to be noted that the tartrates are not very soluble in water, that the solubility is reduced in presence of other salts, and that the scope of the observations would necessarily be more restricted in salt solutions. For this reason, water has been

employed as solvent, and although this procedure is necessarily associated with variations of K_1 and K_2, it is significant that if these coefficients are modified to the same extent by variations in the salt content of the solution, the concentrations of the tartaric acid molecule and of the bitartrate and tartrate ions are not appreciably changed. This does not, however, apply to the hydrogen-ion concentration, but since the catalytic influence of the hydrogen ion in the buffer mixtures is for the most part relatively small, it follows that the variations in K_1 and K_2 can generally be ignored.

Furthermore, since the solutions containing the tartrate buffers are limited in concentration, it would seem permissible, in accordance with previous results (Dawson and Key, J., 1928, 1248), to assume that the catalytic coefficients do not vary appreciably with the salt content of the reaction medium.

The sum total of the observed catalytic effects shows that the reaction velocity is to be represented in general by the equation

$$v = v_h + v_{HT'} + v_{H_2T} + v_{T''} + v_w + v_{OH'} \quad . \quad . \quad (9)$$

in which the partial velocities are those due to the entities represented by the corresponding subscripts. The relative importance of the partial velocities varies enormously, and under certain conditions some of the terms in this equation may be neglected.

Catalytic Effects of Tartaric Acid.—The experiments with solutions of tartaric acid extend over the range $c = 0.005$ to 0.5 mol. per litre. At these concentrations, the second-stage dissociation is inappreciable, and on the assumption that the reaction velocity is represented by $v = v_h + v_{H_2T} + v_{HT'} = k_h[H^\bullet] + k_{H_2T}[H_2T] + k_{HT'}[HT']$, the experimental data may be employed for the derivation of K_1 and k_{H_2T} by the method which has been successfully applied to monobasic acids of widely varying ionisation tendency (cf. Dawson, Hall, and Key, J., 1928, 2844). The equation for the reaction velocity may be put in the form $v/\sqrt{[H_2T]} = (k_h + k_{HT'})\sqrt{K_1} + k_{H_2T}\sqrt{[H_2T]}$, and in accordance with this, it is found that the plot of $v/\sqrt{[H_2T]}$ against $\sqrt{[H_2T]}$ yields a straight line. The slope of this gives the value of k_{H_2T}, and the intercept on the zero ordinate affords a measure of $(k_h + k_{HT'})\sqrt{K_1}$, in which k_h and $k_{HT'}$ are known. The data for the tartaric acid solutions lead in this way to $K_1 = 8.5 \times 10^{-4}$ and $k_{H_2T} = 26.0 \times 10^{-6}$. The higher value of $K_1 = 9.7 \times 10^{-4}$ derived by Ostwald from conductivity measurements (*Z. physikal. Chem.*, 1899, **3**, 370) is no doubt in part due to the use of 320.5 for the mobility of the hydrogen ion whereas the true value is probably not far removed from 350.

The reaction velocities at 25° with an acetone concentration

of 20 c.c. per litre are shown in Table I. The successive horizontal rows give the molar concentration of the acid, the hydrogen-ion concentration, the calculated partial velocities v_h, v_{H_2T}, and $v_{HT'}$, the calculated total velocity $v_{calc.}$, and the observed velocity $v_{obs.}$. The coefficients used for the hydrogen and the bitartrate ions are $k_h = 465 \times 10^{-6}$, $k_{HT'} = 8.5 \times 10^{-6}$, and the velocities are expressed in mols. per litre per minute.

TABLE I.

Catalyst : tartaric acid.

c	0·005	0·01	0·02	0·04	0·05	0·08	0·1	0·15	0·25	0·5
$10^4 . [H^{\cdot}]$	16·8	25·2	37·2	54·2	61·1	78·3	88·0	108·7	141·6	202·0
$10^6 . v_h$ ...	0·78	1·17	1·73	2·52	2·84	3·64	4·09	5·06	6·58	9·39
$10^6 . v_{H_2T}$	0·09	0·195	0·42	0·90	1·14	1·88	2·37	3·62	6·13	12·50
$10^6 . v_{HT'}$	0·01	0·02	0·03	0·05	0·05	0·07	0·08	0·09	0·12	0·17
$10^6 . v_{calc.}$	0·88	1·39	2·18	3·47	4·03	5·59	6·54	8·77	12·8	22·0
$10^6 . v_{obs.}$	0·91	1·40	2·20	3·49	4·03	5·65	6·55	8·80	12·9	22·2

Throughout the entire series the calculated and observed velocities are in close agreement and, as in the case of other acids which have been previously examined, there is no evidence of any change in the values of either the dissociation constant K_1 or the catalytic coefficients. The apparent constancy of K_1 with increasing ionic concentration of the solution is very possibly due to the circumstance that the increase of K_1 which would be expected to result from the increasing magnitude of the interionic force effect is counterbalanced by an opposite effect of the medium due to the increasing concentration of the tartaric acid molecules.

The interionic force effects are shown very clearly when the concentration of the tartaric acid is fixed, and the ionic concentration of the environment is increased by the addition of varying quantities of an inert salt. Table II gives the results obtained with $0.1M$-tartaric acid on the addition of sodium chloride. For such solutions the hydrogen-ion concentration may be derived from

$$[H^{\cdot}] = (v - 0.1k_{H_2T})/(k_h + k_{HT'} - k_{H_2T})$$

in which the variation of k_h with the concentration of the inert salt is taken into account. According to the evidence afforded by previous investigations (cf. Dawson and Key, J., 1928, 1248), the corresponding variations in $k_{HT'}$ and k_{H_2T} are probably small, and these are assumed to have the values already recorded.

The hydrogen-ion concentration having thus been determined, the value of K_1 is given by $K_1 = [H^{\cdot}]^2/(c - [H^{\cdot}])$. The results show that the first-stage dissociation coefficient increases with the salt concentration, passes through a maximum, and then slowly decreases. If K_1^x represents the coefficient in sodium chloride solution

(x mols. per litre) and K_1^0 the coefficient for salt-free solution, the variation may be expressed by

$$\log K_1^x/K_1^0 = 0.54\sqrt{x} - 0.24x \quad . \quad . \quad . \quad (10)$$

In Table II the successive columns give the values of x, the initial reaction velocity v, the catalytic coefficient k_h (from experiments with $0.01M$-hydrochloric acid), and K_1^x obs., obtained as explained above ; the last two give the values of K_1^x/K_1^0 obs. and of K_1^x/K_1^0 calc. derived from the logarithmic formula with $K_1^0 = 8.5 \times 10^{-4}$. This formula, which obviously reproduces satisfactorily the observed variations of K_1^x, is of the same form as that which expresses the connexion between the mass-action dissociation coefficient and the corresponding thermodynamic constant when the activity coefficient $f_\pm$ in the equation $K_1^0 = K_1^x . (f_\pm)^2/f_0$ is evaluated in accordance with the Debye–Hückel theory. The numerical constant (0.54) of the $\sqrt{x}$ term is, however, only about half as large as the constant which is suggested by the latter theory.

TABLE II.

Ionisation of tartaric acid in sodium chloride solutions.

x.	$10^6 . v$.	$10^6 . k_h$.	$10^4 . K_1^x$.	K_1^x/K_1^0 obs.	K_1^x/K_1^0 calc.
0	6.55	465	8.5	1.0	1.0
0.02	6.72	467	9.3	1.09	1.18
0.06	7.12	472	11.0	1.29	1.30
0.1	7.29	478	11.6	1.37	1.40
0.25	7.93	496	14.0	1.65	1.63
0.4	8.33	516	15.0	1.76	1.76
0.5	8.70	530	16.1	1.89	1.83
0.7	9.13	557	16.6	1.95	1.92
1.0	9.64	596	16.9	1.99	1.99
1.5	10.4	663	16.7	2.00	2.00
2.0	11.05	726	16.1	1.90	1.92
3.0	12.08	870	13.6	1.60	1.64

The variation of the first-stage ionisation coefficient of tartaric acid with the salt content of the solvent medium is precisely similar to that already observed with acetic, glycollic, chloroacetic, dichloroacetic, and oxalic acids. For the monobasic acids in this series, the effect of sodium chloride on the ionisation coefficient was based on measurements of the rate of hydrolysis of ethyl acetate, but the value of the coefficient of the $\sqrt{x}$ term in the logarithmic formula is identical with that obtained for tartaric acid from observations on the rate of the acetone–iodine reaction. It may be inferred that the constant a in the formula $\log K^x/K^0 = a\sqrt{x} - bx$ is determined solely by the nature of the ions of the added salt.

Catalytic Effects of Sodium Hydrogen Tartrate.—The study of the catalytic effects produced by acid salts is of particular interest in that the two stages of ionisation are involved. For such solutions it

may be shown that $[H^{\cdot}] = \sqrt{K_1 K_2 [HT']/(K_1 + [HT'])}$, $[H_2T] = [H^{\cdot}][HT']/K_1$, $[HT'] = c - [H^{\cdot}] - 2[H_2T]$ and $[T''] = [H^{\cdot}] + [H_2T]$. If the concentration (c) of the acid salt is large compared with K_1, the first expression reduces to $[H^{\cdot}] = \sqrt{K_1 K_2}$, and if c is small compared with K_1 it reduces to $[H^{\cdot}] = \sqrt{K_2(c - [H^{\cdot}])}$. In so far as the hydrogen ion is responsible for the catalytic effects, it may therefore be anticipated that the connexion between the re-action velocity and the concentration of the acid salt will depend on the relative magnitudes of c and K_1.

The bitartrate solutions examined range from $c = 0.01$ to $c = 0.4$ mol. per litre, from which it follows that c is much greater than K_1 throughout the series and therefore $[H^{\cdot}] = \sqrt{K_1 K_2}$. Although increase in the bitartrate concentration is undoubtedly associated with an increase of both K_1 and K_2, the influence of this is not of much importance since the partial velocity v_h is for the most part only a small fraction of the measured total reaction velocity and the concomitant changes in the concentrations of the chief catalysts, the tartaric acid molecule and the bitartrate ion, are relatively very small; it follows from this that K_1 and K_2 may be regarded as constants without introducing any serious error in the calculation of the total reaction velocities.

In addition to K_1, k_h, k_{H_2T}, and $k_{HT'}$, this calculation requires a knowledge of K_2 and $k_{T''}$. The recorded values of K_2 are not very concordant, but recent measurements of the rate of decomposition of ethyl diazoacetate (Duboux and Frommelt, *J. Chim. physique,* 1927, **24**, 245) in which reaction the catalytic effect appears to be almost entirely due to the hydrogen ion, suggest that the second-stage ionisation constant is not far removed from $K_2 = 3 \times 10^{-5}$, and this value has been adopted. The value of $k_{T''} = 1.0 \times 10^{6}$ is that afforded by our reaction-velocity data for the buffer series $c\text{NaHT} + x\text{Na}_2\text{T}$ (p. 2620). In the bitartrate solutions the catalytic effect of the solvent is not quite negligible for the weaker solutions, and the value $v_w = 0.007 \times 10^{-6}$ (cf. Dawson and Key, J., 1928, 543) has been introduced as a constant term into the reaction velocity equation, which, for this series, becomes $v = v_h + v_{H_2T} + v_{HT'} + v_{T'} + v_w$.

TABLE III.

Catalyst : sodium hydrogen tartrate.

c	0.01	0.02	0.04	0.06	0.08	0.1	0.2	0.3	0.4
$10^6 . v_h$	0.070	0.072	0.073	0.073	0.074	0.074	0.074	0.074	0.074
$10^6 . v_{H_2T}$	0.034	0.069	0.140	0.211	0.283	0.355	0.710	1.07	1.42
$10^6 . v_{HT'}$	0.062	0.123	0.247	0.371	0.495	0.62	1.24	1.85	2.47
$10^6 . v_{T''}$	0.001	0.003	0.005	0.008	0.010	0.014	0.03	0.04	0.055
$10^6 . v_{\text{calc.}}$	0.174	0.274	0.472	0.670	0.870	1.07	2.06	3.04	4.03
$10^6 . v_{\text{obs.}}$	0.178	0.284	0.475	0.680	0.87	1.06	2.06	3.09	4.17

The results obtained for the bitartrate solutions are summarised in Table III. The first horizontal series gives the molar concentration of the bitartrate; the next four show the partial velocities v_h, v_{H_2T}, $v_{HT'}$, and $v_{T''}$, and the last two afford a comparison of the calculated ($v_{calc.}$) and observed ($v_{obs.}$) reaction velocities. From the table it is apparent that the observed and calculated

<div align="center">

FIG. 1.

Reaction velocity for sodium hydrogen tartrate solutions.

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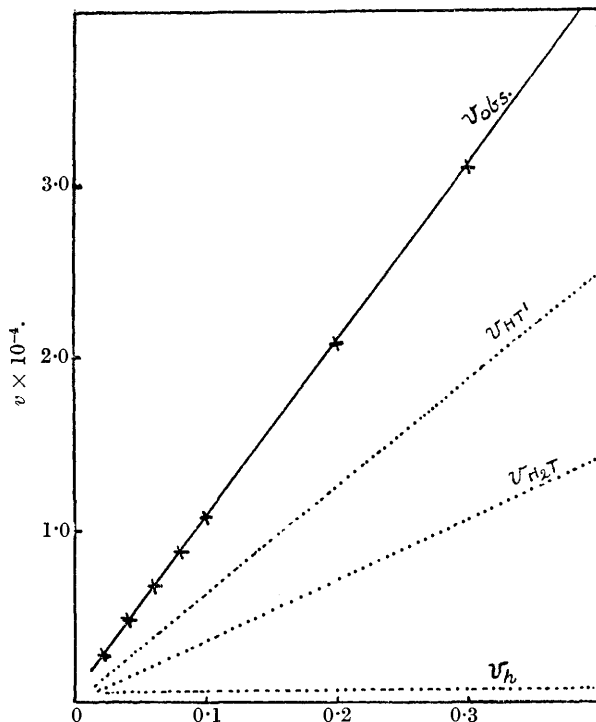
Full curve shows observed velocity : broken curves show calculated partial velocities for the bitartrate ion, the tartaric acid molecule, and the hydrogen ion.

velocities are in close agreement over the entire concentration range, and strong support is thereby obtained for the validity of the above equation.

By combining the expression $[H^{\cdot}] = \sqrt{K_1 K_2}$ with the stoicheiometric relation $[H_2T] + [HT'] + [T''] = c$ and the mass-law expressions for K_1 and K_2, it may be shown that $[H_2T] = [T''] = mc$ and $[HT'] = nc$, where $m = \sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2})$ and $n = \sqrt{K_1}/(\sqrt{K_1} + 2\sqrt{K_2})$. It then follows that the equation for the

reaction velocity in the bitartrate solutions may be written in the form

$$v = k_h\sqrt{K_1 K_2} + [(k_{H_2T} + k_{T''})m + k_{HT'} . n]c + v_w$$

according to which the velocity should be a linear function of the bitartrate concentration c in so far as the latter is not very small. The graph in Fig. 1 shows that the observed velocity follows a linear course over the entire range from 0·01 to 0·4 mol. per litre. The broken curves show the calculated partial velocities $v_{HT'}$, v_{H_2T}, and v_h, and it is clear that the catalytic effects in the more concentrated solutions are almost entirely due to the bitartrate ion and the tartaric acid molecule.

From $K_1 = 8·5 \times 10^{-4}$ and $K_2 = 3·0 \times 10^{-5}$, we obtain $m = 0·137$ and $n = 0·729$, whence $dv/dc = 9·9 \times 10^{-6}$, which agrees closely with the slope of the experimental v–c curve. From this observed slope it would obviously be possible to derive a value for the second-stage ionisation constant K_2.

Catalytic Effects of First-stage Buffer Mixtures.—The experimental data for acid–bitartrate mixtures of the type $cH_2T + xNaHT$ (c constant, x variable) show that the reaction velocity falls at first as x increases, passes through a minimum, and then increases linearly with the bitartrate concentration. From the results, values for k_{H_2T} and $k_{HT'}$ may be derived by methods previously described. These values vary to a small extent with the magnitude of c which is characteristic of the series and it seems probable that this is connected with the formation of tartrate complexes (see p. 2620).

The observed initial velocities for two series of first-stage buffers are shown in Table IV. In these series the partial velocities v_w and $v_{OH'}$ can be neglected, and the calculated velocities are accordingly derived from the equation $v = v_h + v_{H_2T} + v_{HT'} + v_{T''}$.

TABLE IV.

Catalyst : $0·05C_4H_6O_6 + xNaHC_4H_4O_6$.

x	0	0·02	0·04	0·06	0·08	0·1	0·2	0·3	0·4
$10^6 . v_{obs.}$	4·03	2·34	2·12	2·13	2·19	2·35	3·27	4·26	5·30
$10^6 . v_{calc.}$	4·04	2·34	2·14	2·18	2·28	2·42	3·30	4·24	5·20

Catalyst : $0·1C_4H_6O_6 + xNaHC_4H_4O_6$.

x	0	0·02	0·04	0·06	0·08	0·1	0·2	0·3	0·4
$10^6 . v_{obs.}$	6·55	4·36	3·81	3·66	3·72	3·79	4·59	5·58	6·70
$10^6 . v_{calc.}$	6·55	4·36	3·86	3·76	3·80	3·88	4·65	5·52	6·46

In both series, the observed and calculated reaction velocities are in close agreement.

Catalytic Effects of Second-stage Buffer Mixtures.—The second-stage buffers examined were of the type $cNaHT + xNa_2T$ (c constant, x variable). The v–x curve is of the normal type, showing a minimum

and a linear relation at the higher values of x. From this, values of $k_{HT'}$ and $k_{T''}$ may be derived. In consequence of the small value of K_2, the catalytic effect of the hydrogen ion becomes negligible for very small additions of the normal tartrate, and beyond this stage changes in the value of K_2 due to increasing salt concentration may be ignored. The relations for this series of tartrate buffers are thus very similar to those met with in the case of acetate buffers of the same type.

The measured velocities for the series $0.05NaHT + xNa_2T$ are shown in Table V. The catalytic effect of the hydroxyl ion begins to be appreciable at the higher values of x, and the calculated velocities are accordingly derived from the general equation (9) (p. 2614).

TABLE V.

Catalyst : $0.1NaHC_4H_4O_6 + xNa_2C_4H_4O_6$.

x	0	0.02	0.04	0.06	0.1	0.2	0.3	0.4
$10^6 . v_{obs.}$	1.06	1.00	0.98	0.965	0.98	1.04	1.15	1.26
$10^6 . v_{calc.}$	1.07	1.00	0.99	0.99	1.01	1.09	1.19	1.29

The results for other buffer series of this type show the same general features, but the detailed observations need not be recorded since the accuracy of the measurements is limited by the correction for the loss of iodine in the blank (acetone-free) experiments, which is considerable for these solutions. For this reason the value $k_{T''} = 1.0 \times 10^{-6}$ can only be regarded as approximate. On the other hand, it seems to be quite clear that the slope of the linear portion of the v–x curve varies appreciably with the concentration of the bitartrate which is characteristic of each such series. This suggests that the constitution of these solutions is complicated by the formation of tartrate complexes in which the normal tartrate ions are involved; and it is significant that such complex formation has been postulated to account for the anomalous dispersion of tartaric acid and its salts (cf. Astbury, *Proc. Roy. Soc.*, 1923, **102**, 506).

The observations described show clearly that the acetone–iodine reaction is catalysed by undissociated tartaric acid and by the bitartrate and tartrate ions. The catalytic coefficients for these are $k_{H_2T} = 26 \times 10^{-6}$, $k_{HT'} = 8.5 \times 10^{-6}$, and $k_{T''} = 1 \times 10^{-6}$, which compare with $k_h = 465 \times 10^{-6}$. The catalytic effects produced by sodium hydrogen tartrate are almost entirely due to the joint action of the tartaric acid molecule and the bitartrate ion when the concentration of the solution is greater than 0.05 mol. per litre. For such bitartrate solutions the catalytic effect is a linear function of the concentration.

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