Studies of the Rate of Inversion of Sucrose in Aqueous Solutions of Some Strongly Dissociated Acids. Part II.[1] Acidity Constants for Acetylenedicarboxylic and Propiolic Acids

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The rates of inversion of sucrose in dilute aqueous solutions of acetylenedicarboxylic acid and of its monopotassium salt have been measured at 25 °C. The first and second acidity constants have been calculated. The exact values found depend upon the magnitude of the primary kinetic salt effect on the reaction. Measurements have also been made on solutions of propiolic acid. The acidity constant values have been confirmed by pH titration.

THE first part of this work [1] demonstrated that acidity constants with values between 10 and 10^{-3} mol l^{-1} are particularly sensitive to the assumptions made in their calculation from the experimental results. This is likely to be even more important when two equilibria, with overlapping acidity constants, are involved. Acetylenedicarboxylic acid has two fairly strongly acidic hydrogen atoms and is thus a convenient compound for study. The inversion of sucrose is specifically catalysed by hydrogen ions and reasonable assumptions about the primary kinetic salt effect on this reaction enable [1,2] one to calculate the hydrogen ion concentration in the solution. Measurements of the rate of inversion of sucrose in aqueous solutions of acetylenedicarboxylic acid (H_2A) and of its monopotassium salt (KHA) lead primarily to values of the first and second acidity constants respectively, with the other acidity constant only contributing to a minor correction term in each case. Measurements of the rate of inversion in solutions of propiolic (propynoic) acid were also made.

EXPERIMENTAL

Apparatus and Procedure.—Both the apparatus and procedure were as described in Part I.[1] The temperature in the polarimeter tubes was 25·00 ± 0·02 °C measured with a Hewlett–Packard quartz crystal thermometer. Reactions were followed for a period of about 1 day. During this time the concentrations of stock solutions of H_2A and KHA changed slightly due to decarboxylation, but the acidimetric titres fell by only 1% or less during the reaction. The overall experimental error in the rate constants was probably *ca.* 0·5%.

pH Titrations were made with a Radiometer No. 4 pH-meter with the solutions thermostatted to 25·0 ± 0·1 °C. The pH-meter was calibrated with 0·05M-potassium hydrogen phthalate.

Materials.—Fresh stock solutions of H_2A were prepared for each run by passing an 0·1M solution of potassium hydrogen acetylenedicarboxylate (Koch–Light Ltd., purity 99·9% by acidimetric titration) through a column packed with the cation exchange resin Amberlite IR 120 in the hydrogen-ion form. After discarding four bed-volumes no residual potassium was detectable in the effluent with a flame photometer indicating at least 99·99% conversion into the acid. Solutions of KHA were also prepared freshly for each run. All stock solutions were analysed acidimetrically to ±0·01% by the weight titration technique described previously.[1] Propiolic acid (Koch–Light Ltd.) was used without further purification. Aqueous solutions more concentrated than *ca.* 0·1M were slightly coloured and the results of polarimetric measurements on them are less reliable.

RESULTS AND DISCUSSION

The rate constants for the sucrose inversions are given in Table 1.

TABLE 1

First-order rate constants k_{obs} for sucrose inversion in aqueous acid solutions

$HO_2C{\cdot}C{\equiv}C{\cdot}CO_2H$		$HO_2C{\cdot}C{\equiv}C{\cdot}CO_2K$		$HO_2C{\cdot}C{\equiv}CH$	
$\frac{c}{\text{mol l}^{-1}}$	$\frac{10^4 k_{obs}}{\text{min}^{-1}}$	$\frac{c}{\text{mol l}^{-1}}$	$\frac{10^4 k_{obs}}{\text{min}^{-1}}$	$\frac{c}{\text{mol l}^{-1}}$	$\frac{10^4 k_{obs}}{\text{min}^{-1}}$
0·09619	$6{\cdot}78_2$	0·1013	$2{\cdot}08_2$	0·3294	$5{\cdot}1_5$ [a]
0·08154	$5{\cdot}88_8$	0·1013	$2{\cdot}07_1$	0·1767	$3{\cdot}6_4$ [a]
0·04904	$3{\cdot}82_2$	0·09433	$2{\cdot}00_2$	0·1007	$2{\cdot}52_8$
0·04080	$3{\cdot}27_4$	0·07232	$1{\cdot}65_6$	0·0634	$1{\cdot}84_6$
		0·05360	$1{\cdot}35_4$		
		0·04024	$1{\cdot}12_5$		

[a] Reduced accuracy because the solutions were coloured.

Earlier studies [1,2] have established that in solutions of completely dissociated acids the first-order rate constant k for the inversion of sucrose is related to the molarity c of the acid by equation (1) where Z is a constant

$$k = Zc \times 10^{B_j c} \qquad (1)$$

determined by the sucrose concentration and B_j is a constant determined by the anion. The value of Z used was $7{\cdot}46 \times 10^{-3}$ l mol^{-1} min^{-1} and was obtained [1] from measurements on dilute solutions of hydrochloric acid for which [2] $B_j = 0{\cdot}28$ l mol^{-1}.

For inversion in solutions of a weak acid equation (1) is modified to give equation (2) where the summation

$$k = Z[H^+] \times 10^{\Sigma_j B_j c_j} \qquad (2)$$

extends over all anions, each with its own specific B_j value.

The dissociation of acetylenedicarboxylic acid can be represented by

$$H_2A \overset{K_1}{\rightleftharpoons} H^+ + HA^- \overset{K_2}{\rightleftharpoons} H^+ + A^{2-}$$

In the absence of any prior information about the B_j values of the two anions it is convenient to assume that the value for the A^{2-} ion is twice that for the HA^-

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[1] A. D. Pethybridge, *J. Chem. Soc.* (*A*), 1969, 1345 is regarded as Part I.

[2] E. A. Guggenheim and L. A. Wiseman, *Proc. Roy. Soc.*, 1950, **230**, *A*, 17.

anion, an assumption that was successful in describing the inversion of sucrose in hydrogen sulphate media.[1]

For acids with overlapping dissociation constants, measurements on solutions of KHA enable one to calculate K_2 but a small correction involving K_1 is necessary to allow for the formation of H_2A. Conversely, measurements on solutions of H_2A lead to a value of K_1 if the small correction involving K_2 is made to allow for the formation of A^{2-}. In the present work values of K_1 and K_2 were found by an iterative operation as follows. First, an approximate value of K_2 was calculated from the rate constants for solutions of KHA with K_1 set at infinity. This value of K_2 was then used to correct values of K_1 calculated from the rate constants for solutions of H_2A. This value of K_1 was then included in the next calculation of K_2 and so on until the values obtained from successive cycles were sufficiently convergent. In each cycle a value of K_1 or K_2 was calculated from the rate constant in each solution and the mean value of K_1 or K_2 from one cycle was used in the next. Equations (3)—(7) were used, where $Z = 7{\cdot}46 \times$

$$\log[\mathrm{H}^+] = \log k_{\mathrm{obs}} - \log Z - B_j([\mathrm{HA}^-] + 2[\mathrm{A}^{2-}]) \quad (3)$$

$$\log y_{\pm} = -AI^{\frac{1}{2}}/(1 + \rho I^{\frac{1}{2}}) \quad (4)$$

$$I = \tfrac{1}{2}([\mathrm{K}^+] + [\mathrm{H}^+] + [\mathrm{HA}^-] + 4[\mathrm{A}^{2-}]) \quad \text{for KHA solutions} \quad (5a)$$

$$I = \tfrac{1}{2}([\mathrm{H}^+] + [\mathrm{HA}^-] + 4[\mathrm{A}^{2-}]) \quad \text{for H}_2\text{A solutions} \quad (5b)$$

$$K_1 = [\mathrm{H}^+][\mathrm{HA}^-]y_{\pm}{}^2/[\mathrm{H_2A}] \quad (6)$$

$$K_2 = [\mathrm{H}^+][\mathrm{A}^{2-}]y_{\pm}{}^4/[\mathrm{HA}^-] \quad (7)$$

10^{-3} l mol^{-1} min^{-1}, $A = 0{\cdot}5115$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$, I is the ionic strength, and B_j and ρ have selected values. When convergent values of K_1 and K_2 had been obtained the procedure was reversed to calculate values of $[\mathrm{H}^+]$ and hence k_{calc} for each solution from these average dissociation constants and the same values of B_j and ρ. A suitable computer program was written in FORTRAN for these calculations.

As was found previously, there is no unique set of the parameters B_j, ρ, and K_a which gives a best fit of the data. The sets of parameters giving an equally good fit are shown in Table 2 (Δ_1 and Δ_2 are the percentage differences between observed and calculated rate constants for solutions of H_2A and KHA respectively). It is noteworthy that when the parameter ρ is changed while B_j is kept constant, both Δ_1 and Δ_2 show a minimum at the same value of ρ. Changes in ρ, at constant B_j, affect the calculated values of K_2 more than K_1 because the activity coefficient is raised to the fourth power in equation (7), whereas it is only raised to the second power in equation (6). However, for the same value of ρ, K_1 is more sensitive to changes in B_j than is K_2. This is always observed with acids of intermediate strength,[1] and the larger the value of the acidity constant, the greater the effect.

TABLE 2

Values of the parameters B_j, ρ, K_1, and K_2 for the inversion of sucrose in solutions of H_2A and KHA

B_j / l mol^{-1}	ρ / l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$	$10K_1$ / mol l^{-1}	10^3K_2 / mol l^{-1}	Δ_1	Δ_2
0·19	1·9	$2{\cdot}23_6$	4·25	$0{\cdot}1_1$	$0{\cdot}4_7$
0·22	2·0	$2{\cdot}17_3$	4·31	$0{\cdot}1_0$	$0{\cdot}4_7$
0·25	2·1	$2{\cdot}11_5$	4·35	$0{\cdot}1_0$	$0{\cdot}4_6$
0·28	2·2	$2{\cdot}06_1$	4·40	$0{\cdot}1_0$	$0{\cdot}4_6$
0·31	2·3	$2{\cdot}01_2$	4·44	$0{\cdot}1_0$	$0{\cdot}4_5$
0·34	2·4	$1{\cdot}96_2$	4·49	$0{\cdot}1_0$	$0{\cdot}4_5$

Analysis of the rate constants for the inversion in solutions of the monobasic propiolic acid are simpler and follow the pattern described previously.[1] The fit is not particularly good, partly because the most concentrated solutions were coloured, but a typical set of parameters is $B_j = 0{\cdot}31$ l mol^{-1}, $\rho = 2{\cdot}2$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$, $K_a = 0{\cdot}0117$ mol l^{-1} for which $\Delta = 1{\cdot}4$.

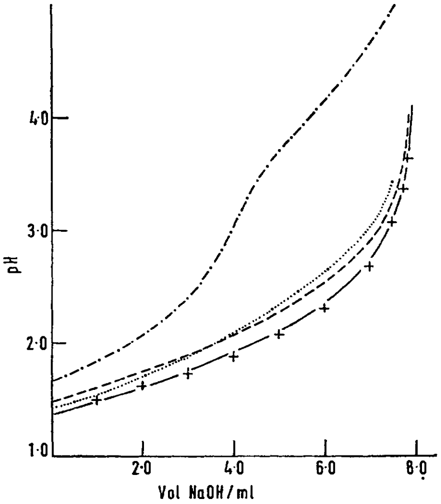

FIGURE 1 Calculated titration curves for 20 ml of 0·05M-H_2A against 0·25M-NaOH:

———— $K_1 = 2{\cdot}01 \times 10^{-1}$ mol l^{-1}, $K_2 = 4{\cdot}36 \times 10^{-3}$ This work
------ $K_1 = 6{\cdot}61 \times 10^{-2}$ mol l^{-1}, $K_2 = 3{\cdot}01 \times 10^{-3}$ Ref. 5
.... $K_1 = 1{\cdot}41 \times 10^{-1}$ mol l^{-1}, $K_2 = 1{\cdot}8 \times 10^{-3}$ Ref. 4
—·—·— $K_1 = 1{\cdot}82 \times 10^{-2}$ mol l^{-1}, $K_2 = 4{\cdot}20 \times 10^{-5}$ Ref. 3
\+ Experimental points

It was mentioned earlier that the acidimetric titres of solutions of H_2A and KHA decreased by *ca.* 1% during 24 h—the duration of a typical kinetic run. This is due to decarboxylation and the formation of the monobasic propiolic acid (HP). The effect of the formation of 0·5% of this acid on the fit and calculated parameters of acetylenedicarboxylic acid was investigated by alteration of the previous program to allow for the formation of HP and P^- and the consequent changes in the equilibrium concentrations of H_2A, HA^-, and A^{2-}. The second-order effects of the formation of HP and P^- on the activity coefficient and the B_j parameter are

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[3] H. W. Ashton and J. R. Partington, *Trans. Faraday Soc.*, 1934, **30**, 598.

[4] M. Charton, *J. Org. Chem.*, 1961, **26**, 735.

[5] R. S. Bottei and W. A. Joern, *J. Chem. Eng. Data*, 1968, **13**, 522.

negligible. This change had no effect on the best fit, nor on the B_j and ρ parameters, but increased K_1 and K_2 by 3×10^{-3} and 6×10^{-5} respectively. These changes are comparable with the experimental error and the effect of the slight decomposition is negligible.

To confirm the values of K_1 and K_2 calculated from the kinetic measurements, pH titrations of 0·05M-H_2A and 0·1M-KHA with 0·25M-sodium hydroxide were made and are compared in Figures 1 and 2 with curves calculated from these values of K_1 and K_2, defining the pH by equation (8). The full lines in Figures 1 and 2

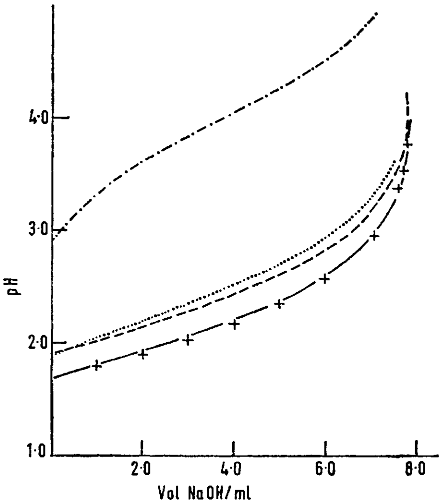

FIGURE 2 Calculated titration curves for 20 ml of 0·10M-KHA against 0·25M-NaOH

———— $K_1 = 2{\cdot}01 \times 10^{-1}$ mol l^{-1}, $K_2 = 4{\cdot}36 \times 10^{-3}$ This work
- - - - - - $K_1 = 6{\cdot}61 \times 10^{-2}$ mol l^{-1}, $K_2 = 3{\cdot}01 \times 10^{-3}$ Ref. 5
········ $K_1 = 1{\cdot}41 \times 10^{-1}$ mol l^{-1}, $K_2 = 1{\cdot}8 \times 10^{-3}$ Ref. 4
—·—·— $K_1 = 1{\cdot}82 \times 10^{-2}$ mol l^{-1}, $K_2 = 4{\cdot}20 \times 10^{-5}$ Ref. 3
+ Experimental points

$$\mathrm{pH} = -\log\,[\mathrm{H}^+]y_{\pm} \qquad (8)$$

were calculated from $K_1 = 0{\cdot}201$ mol l^{-1}, $K_2 = 4{\cdot}36 \times 10^{-3}$ mol l^{-1}, and $\rho = 2{\cdot}2$ $l^{\frac{1}{2}}$ $\mathrm{mol}^{-\frac{1}{2}}$. Use of acidity constants corrected for the formation of HP did not significantly affect the calculated curve. The use of the lower value of $\rho = 1{\cdot}0$ $l^{\frac{1}{2}}$ $\mathrm{mol}^{-\frac{1}{2}}$ improved the fit slightly by raising the curve at the start and lowering it in the middle. However, nearer the end point this value gave a poorer fit, so the choice of ρ is not critical. The agreement between calculated and observed pH values throughout both titration curves is extremely good. The other lines in Figures 1 and 2 were calculated from the following values of the acidity constants taken from the literature:

$K_1 = 1{\cdot}82 \times 10^{-2}$ mol l^{-1} and $K_2 = 4{\cdot}20 \times 10^{-5}$ mol l^{-1} [3];
$K_1 = 1{\cdot}41 \times 10^{-1}$ mol l^{-1} and $K_2 = 1{\cdot}8 \times 10^{-3}$ mol l^{-1} [4];
and
$K_1 = 6{\cdot}61 \times 10^{-2}$ mol l^{-1} and $K_2 = 3{\cdot}01 \times 10^{-3}$ mol l^{-1} [5]

Mansfield and Whiting[6] found $pK_a = 1{\cdot}84$ for propiolic acid from a pH titration using solutions containing 0·1M-NaCl. It is not clear what allowance, if any, had been made for activity coefficients in calculating this value so the agreement with the value of $pK_a = 1{\cdot}93$ found in the present work is acceptable.

Finally it is of interest to compare the acidity constants of the mono- and di-carboxylic acids included in Table 3. The appropriate pK values tabulated in Table 3 are taken from Kortüm's[7] compilation. The large acid-strengthening effect of the triple bond[8] is obvious. Comparison of the pK_1 values of the mono- and di-carboxylic acids shows that the acid-strengthening effect[8] of the second CO_2H group upon the first is transmitted more effectively through the triple bond in acetylenedicarboxylic acid than through the single bond in succinic acid, the values of ΔpK_1 being 1·2 and 0·7 respectively. On statistical grounds one would expect $\Delta pK_1 = 0{\cdot}3$. In the dicarboxylic acids the loss of one proton does not greatly affect the loss of the second when the resultant negative charges are well separated. The observed values of $pK_2 - pK_1$ are 1·2, 1·4, and 1·5 for succinic, fumaric, and acetylenedicarboxylic acids respectively. On statistical grounds one would expect $pK_2 - pK_1 = 0{\cdot}6$ but simple electrostatic theory[9] predicts a value of 1·1. This indicates a reduction of the local dielectric constant or additional interaction between the two carboxylic acid groups through the intervening carbon–carbon bonds.[9] For maleic acid, where the CO_2H groups are adjacent to one another, their mutual influence on the pK values is marked.

TABLE 3

Acid	pK	Acid	pK_1	pK_2
Propionic	4·9	Succinic	4·2	5·6
Acrylic	4·3	Maleic (*cis*)	1·9	6·2
		Fumaric (*trans*)	3·0	4·4
Propiolic	1·9	Acetylenedicarboxylic	0·7	2·4

I thank Miss J. A. Hutton for making some of the kinetic measurements and Professor J. E. Prue for many helpful discussions.

[2/1844 *Received, 4th August*, 1972]

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[6] C. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 1956, 4761.

[7] G. Kortüm, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solutions,' Butterworths, London, 1961.

[8] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.

[9] J. E. Prue, 'Ionic Equilibria,' Pergamon, Oxford, 1966, p. 85.