

1108. *The Acid Strength of Pentane-1,3,5-tricarboxylic Acid.*

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The preparation of pentane-1,3,5-tricarboxylic acid has been investigated; this acid is a tribasic analogue of poly(acrylic acid). Electromotive-force measurements have been carried out on solutions of this acid and its sodium salts, and the intrinsic dissociation constant has been calculated from the results. Two methods of calculation have been used: in one the acid is treated as a polymeric acid; the other involves resolution of the three dissociation constants. The results are compared with the intrinsic dissociation constant of poly(acrylic acid).

PENTANE-1,3,5-TRICARBOXYLIC ACID has been prepared by several authors, but no measurements appear to have been made of its dissociation constants. This is, however, of interest since pentane-1,3,5-tricarboxylic acid is an analogue of poly(acrylic acid), of low molecular weight, in which the repeating unit is $\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot$.

In the case of polymeric acids the strength is usually measured by a dissociation coefficient defined by the equation

$$K = [\text{H}^+][\text{CO}_2^-]/[\text{CO}_2\text{H}] = [\text{H}^+] \cdot \alpha/(1 - \alpha),$$

where α is the fraction of the acid hydrogen atoms which are ionised. The value of K falls as α increases, owing to electrostatic effects, and it is important to estimate the intrinsic dissociation constant K_0 of an individual acid group. Since this corresponds to the dissociation constant of a single carboxyl group in the uncharged acid, it should be obtained by extrapolating K to zero degree of ionisation.

For poly(acrylic acid) a value of 4.28 for $\text{p}K_0 (= -\log K_0)$ was found¹ by extrapolation of Samelson's data² to zero α . On the other hand, an acid analogous to poly(acrylic acid) can be thought of as derived by successive substitution of two $\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ groups in acetic acid; by comparison of the values in the literature for the strengths of acetic and glutaric acid it was argued¹ that the intrinsic strength of pentane-1,3,5-tricarboxylic acid should be given by $\text{p}K_0 = 4.52$.

For a tribasic acid the quantity equivalent to K_0 may be found by determining K as defined above, and extrapolating the result to $\alpha = 0$ as in the case of the polymeric acid. Alternatively, the separate dissociation constants K_1 , K_2 , and K_3 , defined in the conventional manner, may be determined. In this case,³ $K_0 = \frac{1}{3}K_1$. The latter procedure is more accurate.

In the present work electromotive-force measurements have been carried out on a cell without liquid-liquid junction, and the three separate dissociation constants have been resolved, essentially by the method used by Bates and Pinching⁴ for citric acid. The value of K_0 was then found by both the methods outlined above.

EXPERIMENTAL

Synthesis of Pentane-1,3,5-tricarboxylic Acid.—As in Bruson and Riener's cyanoethylation method⁵ but with sodium (1 g.) dissolved in methanol (5 c.c.) as catalyst, diethyl malonate (80 g.) and acrylonitrile (60 g.) were condensed in dioxan (100 c.c.), giving diethyl bis-2-cyanoethylmalonate, m. p. 62°, in nearly quantitative yield.⁶ Hydrolysis by boiling 40% aqueous-ethanolic potassium hydroxide, followed by acidification and recrystallisation of the product from concentrated nitric acid, gave pentane-1,3,3,5-tetracarboxylic acid, m. p. 185—187° (decomp.) (lit.,⁷ m. p. 185—187°), R_F 0.32 in 75:25:1 ethanol-water-28% aqueous ammonia. Decarboxylation of the dry product at 200° gave pentane-1,3,5-tricarboxylic acid, m. p. 114—116° (from acetone) (lit.,⁷ m. p. 114—115°), R_F 0.45⁸ (Found: C, 47.1; H, 6.15 g. Calc. for $\text{C}_8\text{H}_{12}\text{O}_6$: C, 47.1; H, 5.9%), ν_{max} . 1150m, 1250m, 1400m, 1690s, 1740s, 2900—3400m cm^{-1} . Hydrolysis of the dicyano-diester with boiling concentrated hydrochloric acid for 45 hr. gave the tricarboxylic acid directly.⁶

Other reagents were of "AnalaR" grade, and the sodium hydroxide was carbonate-free.

Apparatus.—The hydrogen electrodes were platinised platinum helices; the silver-silver chloride electrodes were prepared electrolytically⁹ from platinum-wire electrodes. Two of each type of electrode were fitted into the cell which was essentially a $4\frac{1}{2} \times 2\frac{1}{2}$ " test tube closed by a large rubber stopper through which were fixed glass sleeves to hold the electrodes. Hydrogen was fed from a cylinder to the hydrogen electrodes through Polythene tubing by way of wash-bottles containing alkaline pyrogallol, very dilute sulphuric acid, and distilled water, at 25°. This purified hydrogen was also passed through a preparatory vessel containing the next solution

¹ Arnold, *J. Colloid. Sci.*, 1957, **12**, 549.

² Samelson, Columbia Univ. Thesis; Microfilms (Ann Arbor, Michigan), Publ. No. 9531 (1954).

³ Britton, "Hydrogen Ions," Chapman and Hall Ltd., London, 1942, 3rd edn., Vol. I, p. 241.

⁴ Bates and Pinching, *J. Amer. Chem. Soc.*, 1949, **71**, 1274.

⁵ Bruson and Riener, *J. Amer. Chem. Soc.*, 1943, **65**, 23.

⁶ Kohler, Goodman, De Graw, and Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 5779.

⁷ Heinke and Perkin, *J.*, 1896, **69**, 1506.

⁸ Westfahl and Gresham, *J. Org. Chem.*, 1956, **21**, 319; Westfahl, *J. Amer. Chem. Soc.*, 1958, **80**, 874.

⁹ Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

to be investigated. The cell and preparatory vessel were both in a water-bath at 25.5°. A Cambridge slide-wire potentiometer reading to 0.1 mv was used.

Procedure.—Measurements were carried out on the cell $H_2(Pt)|H_3A, Na$ salts of H_3A , $NaCl|AgCl, Ag$ where H_3A represents pentane-1,3,5-tricarboxylic acid. The cell solutions were made up in three series: in each series, 10 ml. of 0.1N- H_3A and 10 ml. of sodium chloride, were used, the latter being 1.0N, 0.5N, and 0.1N in series A, B, and C, respectively. In each series, variation of α , the extent of ionisation of the acid, was accomplished by adding varying amounts of N/100- and/or N/10-sodium hydroxide. Each cell solution was finally made up to 100 ml. with boiled, distilled water, to maintain a constant concentration of acid throughout and of sodium chloride in each series. The cell solution was made up by adding solutions to the preparatory vessel through a small hole in the stopper, a carbon dioxide-free hydrogen atmosphere being maintained. The preparatory vessel was identical with the cell used, except that it had no electrodes through the stopper. When it was required to measure the hydrogen-ion activity of the solution, the stopper carrying the electrodes was substituted for that of the preparatory vessel; readings of the e.m.f. were then taken until a steady value was obtained. While the cell was attaining equilibrium (usually about 15 min.), the solutions for the next cell were added to the preparatory vessel. For e.m.f. readings two independent pairs of electrodes were used; if the results disagreed by more than 0.5 mv the faulty electrode was replaced, after having been found by variation of the combination of electrodes. During the e.m.f. readings the passage of hydrogen was stopped.

Methods of Calculation and Results.—By the usual reasoning and conventions it can be shown that each value of the e.m.f., E , of a cell gives a value of the experimental quantity ^{10}pWH :

$$pH - \log f_{Cl^-} = pWH = \frac{(E - E_0)F}{2.303RT} + \log M_{Cl^-} - \frac{1}{2} \log p_H \quad (1)$$

where f is an activity coefficient on the molar scale, M is the molarity, p_H is the partial pressure of the hydrogen, and pH is written for $-\log a_{H^+}$. The results obtained are recorded in the Table.

E.m.f. results.

NaOH (equiv. per equiv. of acid)				NaOH (equiv. per equiv. of acid)				NaOH (equiv. per equiv. of acid)			
E.m.f. (v)	α	pWH	E.m.f. (v)	α	pWH	E.m.f. (v)	α	pWH	E.m.f. (v)	α	pWH
0.100M-NaCl			0.0453M-NaCl			0.0105M-NaCl					
0.000	0.4817	0.0717	3.362	0.000	0.5012	0.066	3.352	0.000	0.5371	0.059	3.317
0.0405	0.4895	0.0937	3.494	0.0421	0.5104	0.088	3.508	0.0425	0.5463	0.084	3.473
0.1049	0.5029	0.137	3.720	0.1063	0.5244	0.133	3.744	0.1063	0.5612	0.127	3.724
0.2025	0.5207	0.219	4.021	0.2179	0.5443	0.230	4.080	0.2121	0.5821	0.223	4.077
0.4805	0.5620	0.484	4.718	0.3210	0.5618	0.327	4.375	0.3189	0.6004	0.324	4.386
0.6414	0.5843	0.643	5.094	0.4773	0.5844	0.480	4.757	0.4804	0.6255	0.482	4.809
0.9046	0.6352	0.905	5.953	0.6397	0.6082	0.641	5.158	0.7961	0.6746	0.799	5.618
				0.7983	0.6329	0.799	5.575	0.8524	0.6866	0.852	5.840
				0.9046	0.6605	0.905	6.041				

Treatment as a polymeric acid. We define

$$K = a_{H^+} a_{CO_2^-} / a_{CO_2H} \quad (2)$$

as in the introduction. Then, if we assume $f_{CO_2H} = 1$, we have

$$pK = pH - \log(N_{CO_2^-} / N_{CO_2H}) - \log f_{CO_2^-} \quad (3)$$

where N is normality.

Here

$$N_{CO_2^-} / N_{CO_2H} = \alpha / (1 - \alpha) \quad (4)$$

where α is the extent of ionisation given by

$$\alpha = (M_{H^+} + M_{NaOH}) / 3M_A \quad (5)$$

Here M_A is the original molarity of H_3A dissolved, M_{NaOH} the molarity of sodium ions derived

¹⁰ Bates, *Chem. Rev.*, 1948, 42, 1.

from sodium hydroxide, and M_{H^+} the molarity of hydrogen ions. The expression for pK may therefore be written:

$$pK = pW - \log [\alpha/(1 - \alpha)] + \log (f_{Cl^-}/f_{CO_3^{2-}}). \quad (6)$$

The last right-hand term in expression (6) could in principle be eliminated by extrapolation to zero ionic strength. The accuracy of the results obtained in the present work does not warrant this, and the term, which is expected to be small, has been disregarded. The equation used is accordingly:

$$pK = pW - \log [\alpha/(1 - \alpha)]. \quad (7)$$

In order to calculate α , values of M_{H^+} have to be estimated from pH values and activity coefficients. The activity coefficients required are those for low concentrations of hydrochloric acid in the presence of both sodium ions and the various carboxylate ions. The total concentration of carboxylic acid is 0.01N, and at the low values of α where activity coefficients are important most of this acid is un-ionised; the effect of carboxylate ions has therefore been neglected. Data are available for the activity coefficients of 0.01M¹¹ and 0.001M-hydrogen chloride¹² in presence of sodium chloride and potassium chloride. Activity coefficients were

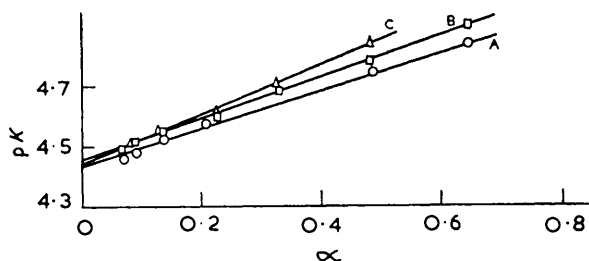
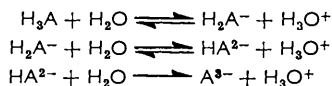


FIG. 1. Plots of pK against α for sodium chloride concentrations (A) 0.1000M, (B) 0.04531M, (C) 0.01047M.

chosen in the light of these data, which indicate that activity coefficients of the acid are close to those for the pure alkali halide at a concentration equal to the total halide concentration of the mixture. The values used for solutions containing 0.1M-, 0.05M-, and 0.01M-sodium chloride were 0.780, 0.826, and 0.904, respectively. The error arising from the uncertainty in the choice of activity coefficients is estimated to be less than 0.4%.

By means of equation (6), the values of pK were calculated for different values of α , and these were plotted against α (Fig. 1). Extrapolation to $\alpha = 0$ gives $pK_0 = 4.43, 4.455,$ and 4.42 for series A, B, and C, respectively. As a mean, we take $pK_0 = 4.44 \pm 0.02$.

Resolution of the Dissociation Constants.—The method is similar to that of Bates and Pinching.⁴ On dissolution of the acid in water, the following equilibria are set up:



Since, at any stage, α represents the fraction of the individual acid groups that have ionised, we have

$$\alpha = (M_{H_2A^-} + 2M_{HA^{2-}} + 3M_{A^{3-}})/3M_A. \quad (8)$$

Also, the concentration of un-ionised acid is given by

$$M_{HA} = M_A - M_{H_2A^-} - M_{HA^{2-}} - M_{A^{3-}}. \quad (9)$$

From the stoichiometric equations (5), (8), and (9) the various concentration terms required in the calculations may be obtained. The ionic strength at any stage is given by:

$$\mu = 3\alpha M_A + M_{H_2A^-} + 3M_{A^{3-}} + M_{NaCl}. \quad (10)$$

¹¹ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 575.

¹² Harned and Åkerlöf, *Phys. Z.*, 1926, 27, 411.

From the definitions of K_1 and of pWH , we derive:

$$\text{p}K_1 = \text{pWH} + \log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-}) + \log (f_{\text{H}_2\text{A}}f_{\text{Cl}^-}/f_{\text{H}_2\text{A}^-}).$$

If we define

$$\text{p}K_1' = \text{pWH} + \log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-}), \quad (11)$$

then at zero ionic strength $\text{p}K_1' = \text{p}K_1$. Values of $\text{p}K_1'$ were found from the e.m.f. data obtained in the neighbourhood of $\alpha = 1/6$. In this region, $M_{\text{A}^{3-}}$ may be neglected and equations (8) and (9) used to express $M_{\text{H}_2\text{A}}$ and $M_{\text{H}_2\text{A}^-}$ in terms of α , M_{A} , and $M_{\text{H}_2\text{A}^{2-}}$. In order to calculate the last term a value of K_2 is required. In the first instance this was taken as equal to the pH at $\alpha = 1/2$, and used without activity coefficients. In this way, $\log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-})$ was calculated. A plot (Fig. 2) of this quantity against pWH for values of α near $1/6$ gives the value of pWH at $\log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-}) = 0$; according to equation (11) this value is equal to $\text{p}K_1'$. The corresponding value of α was then found from a separate plot of $\log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-})$ against α ; hence, μ could be calculated.

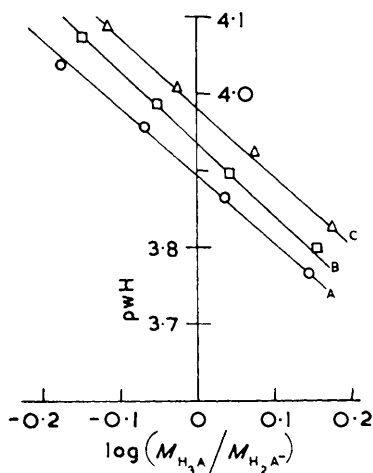


FIG. 2. Plots of pWH against $\log (M_{\text{H}_2\text{A}}/M_{\text{H}_2\text{A}^-})$ for values of α in the neighbourhood of $1/6$, for sodium chloride concentrations (A) 0.1000M , (B) 0.04531M , (C) 0.01047M .

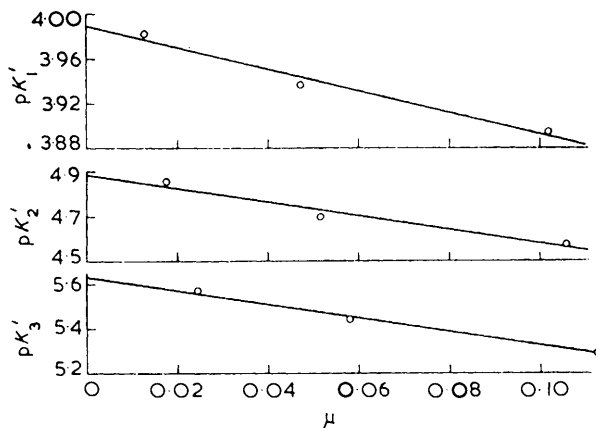


FIG. 3. Graphs $\text{p}K_1'$, $\text{p}K_2'$, and $\text{p}K_3'$ against μ (ionic strength).

This procedure yields $\text{p}K_1'$ as a graphical average found from a range of values of α ; it was repeated for each of the three concentrations of sodium chloride used. The three resulting values of $\text{p}K_1'$ found were extrapolated to $\mu = 0$ to obtain $\text{p}K_1$ (Fig. 3).

In order to calculate $\text{p}K_3$ a procedure similar to that outlined above was used. Data for high values of α were used, where $M_{\text{H}_2\text{A}}$ can be neglected; the preliminary value of K_2 is again required. Values of K_1 and K_3 having been found, they were used to obtain a more accurate value of K_2 . The whole process was then repeated; the second and third calculations of K_2 gave the same value.

Finally, $\text{p}K_0$ was found. Since in a tribasic acid any one of the three hydrogen atoms may ionise first, it may be shown³ that the intrinsic dissociation constant K_0 is given by $K_0 = \frac{1}{3}K_1$, where K_1 is the first dissociation constant. Hence $\text{p}K_0 = \text{p}K_1 + \log 3$. The results obtained from Fig. 3, are

$$\text{p}K_1 = 3.99; \text{p}K_2 = 4.88; \text{p}K_3 = 5.63.$$

Hence $\text{p}K_0 = 4.47$.

These results are considered to be accurate to ± 0.02 unit.

DISCUSSION

Of several methods reported in the literature for the synthesis of pentane-1,3,5-tricarboxylic acid, the cyanoethylation of diethyl malonate⁵ seemed most suitable. The product was analytically pure, and homogeneous by the criterion of paper chromatography. A second method of preparation, involving cyanohydrin formation from the readily accessible diethyl γ -ketopimelate, was attempted as well, partly because the route would be new, and partly because the intermediate α -hydroxy-acid was required for dissociation-constant studies in relation to citric acid. The ketonic group proved, however, unreactive towards hydrogen cyanide under a variety of conditions, an effect which must be attributed to intramolecular interference by one of the ethoxycarbonyl groups (or carboxylate ions when the acid was employed).

The value of pK_0 obtained by extrapolation (4.44) agrees reasonably well with the value of 4.47 for $-\log(K_1/3)$, showing that the two methods of calculation yield the same quantity. The result for pK_0 also agrees with the value 4.52 predicted¹ from the data for acetic and glutaric acid. On the other hand, the value of pK_0 found for polyacrylic acid by extrapolation¹ was 4.28, which does not agree with the result for the tribasic analogue. Since at low degrees of ionisation internal hydrogen bonding decreases the apparent strength of a carboxylic acid,¹³ our results may indicate that less hydrogen bonding occurs in the polymeric than in the tribasic acid.

The close agreement between the measured and the predicted values for the tribasic acid support the value 4.25 estimated¹ by similar arguments for the tricarboxylic analogue of poly(methacrylic acid), 4-methylheptane-2,4,6-tricarboxylic acid. This value agrees with the value of pK_0 for poly(methacrylic acid) obtained by extrapolation. It would, therefore, be of interest to synthesise this other tribasic acid and to determine its strength directly.

A statistical treatment³ shows that for the tribasic acid, if there were no interaction between neighbouring carboxyl groups, then $K_1/K_2 = K_2/K_3 = 3$. The values found in this investigation were: $K_1/K_2 = 7.8$; $K_2/K_3 = 5.6$. The ratios are removed from ideality by a factor of only two. This means that interaction between the carboxyl group is very small. Further, the relatively small difference between K_1/K_2 and K_2/K_3 indicates a near equivalence of all three carboxyl groups, although the middle one has an environment different from that of the other two.

For a dibasic acid whose acid groups behave independently $K_1/K_2 = 4$. Comparison of the ideality in behaviour of a dibasic acid with a tribasic acid may be made by comparison of the ratios $K_1/4K_2$ for the dibasic acid with $K_1/3K_2$ for the tribasic acid. For glutaric acid $K_1/4K_2 = 11.8/4 = 2.8$,¹⁴ and for pentane-1,3,5-tricarboxylic acid $K_1/3K_2 = 7.8/3 = 2.6$. This fairly close correspondence seems to show that the degree of interaction between neighbouring carboxyl groups is of the same order in glutaric as in pentane-1,3,5-tricarboxylic acid. The success obtained in predicting the acid strength of pentane-1,3,5-tricarboxylic acid by the method of adding successive $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ units is thus understandable.

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¹³ Laskowski and Scheraga, *J. Amer. Chem. Soc.*, 1954, **76**, 6305.

¹⁴ *Pure Appl. Chem.*, 1961, **1**, Nos. 2-3.