Aqueous Dissociation of Dihydroxycyclopropenone (Deltic Acid)

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Deltic acid ($H_2C_3O_3$) dissociates in water with pK_1 2.57 ± 0.04 and pK_2 6.03 ± 0.06 at 25°, which values indicate it is a considerably weaker acid than the other series members dihydroxycyclobutenedione ($H_2C_4O_4$) and dihydroxycyclopentenetrione ($H_2C_5O_5$).

A RECENT synthesis of dihydroxycyclopropenone[1] (deltic acid, $H_2C_3O_3$) has provided the three-carbon member of the cyclic oxocarbon acid series of which the anions are noted for their aromatic character[2] and some of the acids for their high acid strengths: dihydroxycyclobutenedione ($H_2C_4O_4$) pK_1 0.54 ± 0.06,[3] pK_2 3.48 ± 0.02,[4] and dihydroxycyclopentenetrione ($H_2C_5O_5$) pK_1

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[1] D. Eggerding and R. West, *J. Amer. Chem. Soc.*, 1975, **97**, 207.

[2] R. West and D. L. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 2577.

[3] L. M. Schwartz and L. O. Howard, *J. Phys. Chem.*, 1971, **75**, 1798.

[4] L. M. Schwartz and L. O. Howard, *J. Phys. Chem.*, 1970, **74**, 4374.

0.80 ± 0.08,[5] pK_2 2.24 ± 0.01.[5] To discover if the high acid strength extends to deltic acid we have made pH potentiometric titrations of aqueous solutions of both deltic acid with NaOH and the salt $Li_2C_3O_3$ with HCl.

EXPERIMENTAL

Samples of both $H_2C_3O_3$ and $Li_2C_3O_3$ were generously supplied by D. Eggerding and R. West of the University of Wisconsin. Their synthesis of $H_2C_3O_3$ is reported elsewhere[1] and $Li_2C_3O_3$ was prepared by reaction of bis(trimethylsiloxy)cyclopropenone with lithium t-butoxide.[6] We used these samples without purification. The titration endpoints revealed that the lithium salt was monohydrated and that the sample contained *ca.* 5% of a basic impurity, while deltic acid was anhydrous and free of impurity to within the accuracy of our equivalent weight determinations. An Orion model 801 digital pH meter was equipped with micro-glass and micro-calomel electrodes and standardized by a 'two buffer' method using 0.1M-HCl and a 1 : 1 phosphate mixture.[7] In a typical experiment, the meter was standardized at the appropriate temperature by utilizing measured portion of the buffer in a cell thermostatted to ±0.2°. The meter standardization was rechecked at the completion of each experiment and seldom differed from the initial settings by more than 0.005 pH units. Titrations of $H_2C_3O_3$ were carried out between 15 and 35° with some decomposition being noted at 30 and 35° but not at 25 or less within *ca.* 3 h. An attempted titration at 45° resulted in decomposition within minutes. One $H_2C_3O_3$ sample at 25° was titrated beyond the second equivalence point with NaOH, then back titrated with an excess of HCl, and then back again with NaOH. The stability of deltic acid and its anions was established at this temperature in that the three pK_1 and pK_2 values calculated from these data were in agreement to within 0.01 and 0.06, respectively.

RESULTS AND DISCUSSION

The pK values were calculated from the well known stoicheiometric and equilibrium relationships of a dibasic acid in aqueous solution. Concentrations were expressed as molarities and molar activity coefficients of ionic species were estimated using the Debye–Hückel equation with ion-size parameters of 4.5 and 9 Å for deltate anions and hydronium, respectively. The temperature dependencies of the other Debye–Hückel parameters were taken from the Robinson and Stokes[8] tabulation. pK Values were calculated for solutions corresponding to each recorded pH and volume. Since the pK values for the primary and secondary dissociations were sufficiently well separated, it was possible to derive pK_1 values solely from solutions before the first equivalence point in the $H_2C_3O_3$ titration (or between the two equivalence points in the $Li_2C_3O_3$ titration) and to derive pK_2 from solutions between the $H_2C_3O_3$ titration equivalence points (or before the first equivalence point of the $Li_2C_3O_3$ titration). In any case, an iterative calculation was required to solve the set of equations to determine ionic strength, activity coefficients, and hydronium concentration in each solution from the pH and solution volume. It was apparent from an inflection at the beginning of the titration that the $Li_2C_3O_3$ sample contained a basic impurity amounting to *ca.* 5%. Since the small quantity of material available to us precluded a purification step, we deduced from the initial pH values that the identity of the impurity was lithium carbonate and thus compensated each solution calculation for the presence of carbonate–carbonic acid equilibria. The ultimate justification for this procedure is that pK values calculated in this manner were in close agreement with pK values calculated from the $H_2C_3O_3$ titrations for which impurity compensation was not necessary. In a manner described previously,[5] maximum probable uncertainties were calculated for the computed pK values by estimating sources of determinate and/or random errors in the experimental data and the activity coefficient correlations. This estimate yielded ±0.04 and ±0.06 for pK_1 and pK_2, respectively.

The results are shown in Table 1. Although the trend of pK values with temperature is not clear, it appears that pK_1 may be at a minimum near 25° and that pK_2 is virtually independent of temperature over the experimental range. If these conclusions are true, then the standard enthalpies of both dissociations are nearly zero, which value leads to estimates of the standard entropies of dissociation of −12 and −27 cal mol^{-1} K^{-1} for the first and second dissociation, respectively. In Table 2, these values are shown in comparison to the corresponding thermodynamic quantities of the four and five carbon homologues. Deltic acid is a decidedly weaker acid in both dissociations. From our $\Delta H_2°$ and $\Delta S_2°$ values for deltic acid, it appears that the more positive enthalpy

TABLE 1

Deltic acid dissociation constants from pH potentiometric titrations. Estimated probable uncertainties are ±0.04 and ±0.06 for pK_1 and pK_2, respectively

Temp. (°C)	pK_1	pK_2
15	2.64	5.97
20	2.63	5.94
25	2.57, 2.56, 2.57 [a]	6.00, 6.06, 6.01 [a]
25	2.57 [b]	6.03 [b]
30	2.70	5.96
35	2.84	5.95

[a] A single sample of H_2CO_3 with two back titrations. [b] $Li_2C_3O_3$ titration. All other entries are $H_2C_3O_3$.

TABLE 2

Standard thermodynamic properties of aqueous dissociation of oxocarbon acids at 25°

	$H_2C_3O_3$ [a]	$H_2C_4O_4$ [b]	$H_2C_5O_5$ [c]
pK_1	2.57 ± 0.04	0.54 ± 0.06	0.80 ± 0.08
$\Delta H_1°$/kcal mol^{-1}	~0	−1.49 ± 0.12	+3.9 ± 2.2
$\Delta S_1°$/cal K^{-1} mol^{-1}	~−12	−7.5 ± 0.7	+10 ± 8
pK_2	6.03 ± 0.06	3.48 ± 0.02	2.24 ± 0.01
$\Delta H_2°$/kcal mol^{-1}	~0	−3.0 ± 0.5	−3.0 ± 0.3
$\Delta S_2°$/cal K^{-1} mol^{-1}	~−27	−26.1 ± 1.6	−20 ± 1

[a] This work. [b] Refs. 3 and 4. [c] Ref. 5.

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[5] L. M. Schwartz, R. I. Gelb, and J. O. Yardley, *J. Phys. Chem.*, 1975, **79**, 2246.

[6] R. West, personal communication.

[7] R. G. Bates, 'Determination of pH Theory and Practice,' Wiley, New York, 1973, 2nd edn.

[8] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1965, 2nd edn. (revised).

change compared with $H_2C_4O_4$ and $H_2C_5O_5$ is the main reason for the weaker second dissociation. This may be caused by a decreased stability of the deltate dianion due to ring strain. On the other hand, pK_1 of deltic acid is larger than that of $H_2C_4O_4$ or $H_2C_5O_5$ because of a more negative $\Delta S_1°$ value. The more positive $\Delta S_1°$ values of $H_2C_4O_4$ and $H_2C_5O_5$ have been attributed to the two effects: (a) an unusually high degree of water structuring around the uncharged acid molecules or (b) an unusually low degree of water structuring around the monoanions perhaps as a result of charge delocalization. The trend of increasing $\Delta S_1°$ with increasing ring size favours the latter of these effects. However the $\Delta S_1°$ values, themselves, seem abnormally positive, which might be ascribed to the former effect.

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