Ionization Constants of Acetylenedicarboxylic Acid

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The first and second ionization constants of acetylenedicarboxylic acid were determined at various temperatures and ionic strengths in aqueous solution using a potentiometric titration technique.

THE LITERATURE VALUES of the ionization constants of acetylenedicarboxylic acid in aqueous solution are not consistent, and were determined at only one temperature. Thus, Ashton and Partington (*2*) report values of 1.82×10^{-2} and 4.20×10^{-5} for K_{a_1} and K_{a_2}, respectively. Charton (*5*), however, extrapolated from data obtained by Dondon (*6*) in ethanol- or methanol-water solutions and listed the values 7.07×10^{-2} and 3.55×10^{-3} for K_{a_1} and K_{a_2}, respectively, for aqueous solutions. The discrepancy in the two sets of values has been attributed to the fact that Ashton and Partington were studying the dihydrate of the acid, while Dondon worked with the anhydrous salt.

Since the present authors were studying the chromous reduction of acetylenedicarboxylic acid (*4*) and the ionization constants appeared in the rate law for the reaction, it was decided to determine the ionization constants of the acid directly in aqueous solution at various temperatures and ionic strengths.

EXPERIMENTAL

Water used in the determinations was run through a deionizer, distilled from alkaline permanganate, and finally run through a Barnstead No. 8902 mixed-bed deionizer, which gave a pH of 6.8 to 7.2. All solutions were degassed with prepurified nitrogen which was bubbled through two chromous sulfate towers. Acetylenedicarboxylic acid was prepared from the monopotassium salt (Eastman White Label) by the method of Truce and Kruse (*8*), and recrystallized from ether-petroleum ether (30° to 60° C.). Neutralization equivalents of 114.3 and 114.6 were obtained (calculated 114.1). Potassium chloride was Baker and Adamson reagent special for calomel electrodes, No. 2059. The sodium hydroxide solutions were prepared carbonate-free from Fisher No. S-318 electrolytic pellets, and standardized against primary standard grade potassium acid phthalate (J. T. Baker).

Two vessels were thermostated to ±0.01°, one for the titration and the other for the buffer solution. The latter was a standard phthalate buffer—i.e., 0.05 molal potassium acid phthalate—prepared according to directions given by Bates (*3*). Titrations were performed with a microburet at three temperatures. A Corning Model 12 pH meter was used, with a Beckman No. 41263 glass electrode and Beckman No. 30170 calomel reference electrode. The acetylenedicarboxylic acid solution and the KCl solution were added to the titration vessel, and the mixture was degassed for 20 minutes. The NaOH solution (0.1360*M* for the 0.0100*M* acid; 0.6808*M* for the 0.0500*M* acid) was added with stirring in 0.5-ml. increments, and readings of the pH to the third decimal place were taken after 30 seconds. Volume corrections were made, and the data analyzed by the method of Noyes (*7*) as described by Albert and Serjeant (*1*). The equations used to calculate K_{a_1} and K_{a_2} were:

$$K_{a_1} = \frac{Y_1Z_2 - Y_2Z_1}{X_1Y_2 - X_2Y_1} \quad \text{and} \quad K_{a_2} = \frac{X_1Z_2 - X_2Z_1}{Y_1Z_2 - Y_2Z_1}$$

where X_1, Y_1, and Z_1 refer to readings obtained at the beginning of the titration and X_2, Y_2, and Z_2 refer to those obtained near the end. X, Y, and Z are defined by

$$X = [\mathrm{H}^-]\{B - C + [\mathrm{H}^-]\}$$
$$Y = 2C - \{B + [\mathrm{H}^+]\}$$
$$Z = [\mathrm{H}^-]^2\{B + [\mathrm{H}^-]\}$$

where C is the total concentration (all species) of the acid being titrated and B is the concentration of the base that has been added. The computations were performed on the Notre Dame Univac 1107 computer.

Table I. Ionization Constants of Acetylenedicarboxylic Acid in Aqueous Solution

[Acid][a], $M \times 10^2$	μ[b], M	$T°$, ° C.	pK_{a_1}	K_{a_1}, $M \times 10^2$	pK_{a_2}	K_{a_2}, $M \times 10^3$
1.00	[c]	18.8	1.040 ± 0.027[d]	9.12	2.495 ± 0.007[d]	3.20
1.00	0.50	18.8	1.089 ± 0.016	8.15	2.046 ± 0.009	9.00
5.00	0.50	18.8	0.876 ± 0.037	13.3	1.896 ± 0.027	12.7
1.00	[c]	28.2	1.229 ± 0.011[d]	5.90	2.533 ± 0.016[d]	2.93
1.00	0.50	28.2	1.203 ± 0.010	6.27	2.097 ± 0.008	8.01
1.00	0.80	28.2	1.025 ± 0.015	9.45	2.029 ± 0.007	9.36
5.00	0.50	28.2	0.917 ± 0.013	12.1	1.952 ± 0.021	11.2
5.00	0.80	28.2	0.781 ± 0.012	16.6	1.907 ± 0.011	12.4
1.00	[c]	36.6	1.295 ± 0.006[d]	5.07	2.576 ± 0.007[d]	2.66
1.00	0.50	36.6	1.212 ± 0.006	6.15	2.116 ± 0.009	7.56
5.00	0.50	36.6	0.942 ± 0.004	11.4	2.004 ± 0.012	9.93

[a] At half-neutralization. [b] Adjusted with KCl. [c] No added salt. [d] Thermodynamic values, corrected for ionic strength.

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For the titrations in which KCl was not added, the ionic strength was estimated and thermodynamic values for pK_a were calculated from the equations (*1*)

$$pK^T_{a_1} = pK_{a_1} + \frac{0.505\ (\mu)^{1/2}}{1 + 1.6\ (\mu)^{1/2}}$$

and

$$pK^T_{a_2} = pK_{a_2} + \frac{1.515\ (\mu)^{1/2}}{1 + 1.6\ (\mu)^{1/2}}$$

RESULTS AND DISCUSSION

The calculated values of the ionization constants are listed in Table I. The precision of the pK_a values is the standard deviation of five sets of two data points for each titration. In the case of the solutions in which KCl was added, the constants are concentration- and ionic strength-dependent, and are not thermodynamic values. Since the Debye-Hückel law does not hold in solutions of high ionic strength, no corrections were attempted.

The results of the titration at 28.2° C. in which no KCl was added ($K_{a_1} = 5.90 \times 10^{-2}$ and $K_{a_2} = 2.93 \times 10^{-3}$) are similar to those reported by Charton (*5*) at 25° C. (7.07×10^{-2} and 3.55×10^{-3}). Apparently, the early work of Ashton and Partington was not accurate.

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Thermochemical Study of the Structures of 1,2-, 2,1-, and 4,1-Nitrosonaphthols

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The heats of combustion and heats of sublimation of 1,2-, 2,4-, and 4,1-nitrosonaphthols were measured. The calculated heats of atomization and heats of combustion (using McGinn's self-consistent set of hydridized bond contributions to heats of combustion) for both the oxime and the nitroso structures were compared with the observed values. The calculations favor the nitroso forms for 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, and 4-nitroso-1-naphthol.

VARIOUS PROPOSALS based on absorption spectra, reduction potentials, and other physical properties have been put forward concerning the molecular structure of the nitrosophenols and the nitrosonaphthols.

Havinga and his associates (*13, 27*) have shown, on the basis of electronic spectra, that *p*-nitrosophenol exists in solution in tautomeric equilibrium with the quinone oxime while only the oxime form exists in the solid state, and that the oxime form of 4-nitroso-1-naphthol is the predominating tautomer in solution. Burawoy and his associates (*6*) have similarly shown that *o*-benzoquinone oxime forms solutions in which the phenolic tautomer prevails, but that 1-nitroso-2-naphthol exists in the oxime form only. Jaffe (*15*) has calculated by the molecular-orbital method that the oxime form of *p*-nitrosophenol should be the more stable.

Hadzi (*12*) investigated the infrared spectra for *p*-nitrosophenol and 4,1-, 2,1-, and 1,2-nitrosonaphthols and found that the oxime formulation correctly represents the structure of these compounds in the solid state, and predominates in their chloroform solutions. However, 2,1-nitrosonaphthol seems to exist in the chelated nitrosoform in solution in carbon tetrachloride. Amstutz, Hunsberger, and Chessick (*1*) found that 1-nitroso-2-naphthol does not show any normal OH vibration and attributed this to chelation of the compound.

On the other hand, Baltazzi (*2*) concluded from his infrared spectral studies that 4,1-nitrosonaphthol is actually a phenol and that the 1,2- and 2,1-nitrosonaphthols are oximes. His conclusions are based on a comparison of the spectra of the alcoholic solutions of 1,2-, 2,1-, and 4,1-nitrosonaphthols with those of their corresponding methyl oxime ethers and their acyl substitution compounds.

The dipole moment studies of Lutskiĭ and Kochergina (*21*) provide evidence for the presence of an intramolecular hydrogen bond in 1,2- and 2,1-nitronaphthols and its absence from 1,2- and 2,1-nitrosonaphthols, and indicate that in benzene 4,1-nitrosonaphthol has mainly a phenolic structure and that 1,2- and 2,1-nitrosonaphthols in benzene and in dioxane have a similar structure.

Because of the widely differing conclusions cited above, additional evidence as to the structures of these compounds, particularly in the solid state, is needed.

EXPERIMENTAL

Materials. Benzoic acid, National Bureau of Standards sample 39h.