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Aqueous Dissociation of Acetylenedicarboxylic Acid

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The two dissociation constants of aqueous acetylenedicarboxylic acid have been determined by pH potentiometry between 15 and 50 °C. The results indicate that this acid is stronger than previously thought; i.e., $pK_{a1} = 0.656 \pm 0.036$ and $pK_{a2} = 2.336 \pm 0.014$ at 25 °C. Standard entropies and enthalpies of dissociation are also determined.

The most recently published report of determinations of acid dissociation constants of acetylenedicarboxylic acid (2-butynedioic acid, to be denoted as H_2A) was by Bottei and Joern (*1*) in this journal. These authors compare their determinations with earlier values of Ashton and Partington (*2*) and of Charton (*3*) and note some discrepancies. In the course of our investigations of complexes of strong organic acids with acid-base indicators (*4*) and complexes of dicarboxylic acids with cyclodextrin, we too required accurate values of acid dissociations of H_2A and attempted to confirm the pH potentiometric determinations of Bottei and Joern. Although we titrated the monopotassium salt KHA with HCl, we should have obtained the same values as these workers who used H_2A and NaOH, but the results are at variance. Because the acid dissociation properties of H_2A are important to the understanding of aquation phenomena of relatively strong organic acids, we hereby report the results of our determinations of acid dissociation pK_a's between 15 and 50 °C and standard entropies and enthalpies of dissociation derived from these.

Experimental Section

Acetylenedicarboxylic acid monopotassium salt (Gold Label) was obtained from Aldrich Chemical Co. Vacuum dried samples of the salt titrated with standardized NaOH consistently yielded equivalent weights between 152 and 153 (FW = 152.15) and ^{13}C NMR spectra obtained under high S/N (> 100:1) conditions revealed no spurious resonances that might be due to impurities. However, we did find that aqueous KHA solutions decomposed at ambient temperature with a reduction in titer of a few percent per day, probably a decarboxylation reaction. In order to investigate this decomposition, we made experiments where 1:1 molar mixtures of HCl with KHA were allowed to stand at elevated temperatures under anaerobic conditions. In such solutions, gas evolution was noted and the solution titer decreased to about half the initial value. This behavior seems to suggest a decarboxylation reaction resulting in formation of propargylic acid. Therefore, we took the precaution of preparing each KHA solution immediately before use.

pH measurements employed an Orion Model 801 pH meter equipped with conventional glass and reference electrodes. The meter was calibrated with 0.100 F HCl solutions according to Bates (*5*); the calibration was often rechecked after each titration and never found to have drifted more than 0.002 pH. Recorded pH values never differed from the calibration setting by more than 0.8 pH. Solutions were allowed to reach thermal equilibrium as indicated by pH readings stable to ±0.001 pH for 10 min, and this required standing times typically 30 min to 1 h.

In order to investigate possible anomalous ionic strength effects in this system, we performed additional experiments with solutions containing ~0.2 F KHA and 0.3 F added KCl to adjust the ionic strength near 0.5 M. The results of these experiments were 0.69 and 2.29 for pK_{a1} and pK_{a2}, respectively at 25 °C. While these values are probably uncertain to ±0.05 pK units as a result of errors in activity coefficient estimation, they seem sufficiently close to the entries in Table I ($pK_{a1} = 0.656$ and $pK_{a2} = 2.336$) to rule out any anomalous concentration or ionic strength effects.

Table I. Estimates of pK_{a1} and pK_{a2} for Acetylenedicarboxylic Acid at Various Temperatures

T, °C	pK_{a1}	pK_{a2}
15^b	0.712 ± 0.034^a	2.296 ± 0.014^a
18.8^c	1.040 ± 0.027	2.495 ± 0.007
25^b	0.656 ± 0.036^a	2.336 ± 0.014^a
25^d	1.150	2.450
25^e	1.740	4.377
28.2^c	1.229 ± 0.011	2.533 ± 0.016
30^b	0.715 ± 0.037^a	2.371 ± 0.015^a
36.6^c	1.295 ± 0.006	2.576 ± 0.007
40^b	0.680 ± 0.033^a	2.437 ± 0.013^a
50^b	0.597 ± 0.036	2.540 ± 0.013^a

[a] Uncertainties quoted are joint parametric uncertainty limits (*7*). [b] This work. [c] Thermodynamic values of Bottei and Joern (*1*). [d] Reference 3. [e] Reference 2.

Treatment of Data

A previous communication (*6*) details an elaborate procedure for treatment of the titration data which was shown to yield highly accurate and precise pK_a values for such standards as acetic and tartaric acids. The method involves numerical solution of a set of model equations by iterative nonlinear regression. The model equation represents the equilibria, conservation relationships, and activity coefficient correlations which describe the aqueous solutions for which titration data are recorded. Due consideration is given to the effect of statistical uncertainties in both the pH and titrant volume data on the least-squares weighting factors. Since the model equations for the dibasic acid H_2A are the same as those of the example (rhodizonic acid) used in ref 6, there is no need to reproduce them here. It is sufficient to report that 50-mL samples of KHA solutions (~0.05 F) prepared as described above were titrated with standardized 0.500 F HCl. About 15 aliquots of titrant were added to provide in total a small excess of HCl. Because of the relatively low pK_a values of H_2A, the initial 0.05 F KHA solutions contained a large proportion of the dianion A^{2-} so that during the titration the first few solutions containing primarily A^{2-} and HA^- served to establish pK_{a2} while the later solutions served to establish pK_{a1}. However, the model equations did not categorize the data points for pK_{a1} or pK_{a2}; each data point was used to determine both constants simultaneously.

Results of these experiments and calculations are given in Table I where pK_a values found by others are listed for comparison. A discussion of results follows in the next section. Here we call attention to the statistical uncertainties quoted for our pK_a values in Table I. These uncertainties are "joint parametric uncertainty intervals" (JPUI) which measure accounts for the interdependence of parameters determined simultaneously (*7*) and which are a more conservative estimate of uncertainty than either standard error estimates or nonsimultaneous confidence intervals. A sample calculation will serve as an illustration. At 25 °C we recorded 15 data points and determined the two parameters pK_{a1} and pK_{a2} simultaneously from these. The

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Table II. Temperature Dependences of pK_a Values between 15 and 50 °C and Standard Enthalpies and Entropies of Dissociation

	primary dissociation[a]	secondary dissociation[a]
empirical dependence on temp	$pK_{a1} = (237. (\pm 132.)/T) - 0.103 (\pm 0.435)$	$pK_{a2} = (-547. (\pm 43.)/T) + 4.19 (\pm 0.14)$
$\Delta H°$, kcal mol^{-1} [b]	+1.1 (±0.6)	−2.5 (±0.2)
$\Delta S°$, cal mol^{-1} K^{-1} [c]	+0.6 (±2)	−19.3 (±0.6)

[a] Uncertainties in parentheses are standard error estimates of the parameters based on scatter of data points from the line. [b] From pK_a vs. T^{-1} lines. [c] From $T(pK_a)$ vs. T lines.

nonlinear regression yielded $pK_{a1} = 0.656$ and a corresponding standard error estimate $SE(pK_{a1}) = 0.013$. The JPUI is calculated as $2(PF_\alpha)^{1/2}$ SE, where $P = 2$ parameters and $F_\alpha = 3.80$ is the variance ratio F statistic for a 95% confidence level $\alpha = 0.05$ and 2 and 13 degrees of freedom. This yields JPUI $(pK_{a1}) = 0.072$, and since this interval is symmetrical about pK_{a1} we quote 0.656 ± 0.036 in Table I which implies joint parametric uncertainty limits of 0.692 and 0.620. By the same procedure we find joint parametric uncertainty limits of 2.350 and 2.322 for pK_{a2}. These limits can be interpreted crudely as follows: If a large number of replicate experiments are performed in an identical manner and the data from these are treated the same way to yield pairs of pK_{a1}, pK_{a2} values, then for at least 95% of the replications the true (but unknown) pK_{a1} value can be expected to be between 0.692 and 0.620 and at the same time the true pK_{a2} value can be expected between 2.350 and 2.322.

To determine standard entropies and enthalpies of H_2A dissociation, we find that plots of pK_a vs. T^{-1} and $T(pK_a)$ vs. T are linear between 15 and 50 °C and so fit least-squares straight lines to all four plots. The pK_a vs. T^{-1} lines are given in Table II. From the slopes of these lines and the well-known relationships $(\partial pK/\partial T^{-1}) = \Delta H°/2.303R$ and $(\partial T(pK)/\partial T) = \Delta S°/2.303R$, we calculate the thermodynamic parameters shown in Table II. Uncertainties quoted there are standard error estimates which are based on the scatter of the five data points about the respective least-squares line.

Discussion

We note that at all temperatures our pK_a values are lower than those of Bottei and Joern. The discrepancies are about 0.5 for pK_{a1} and 0.2 for pK_{a2} and neither may be attributed to statistical uncertainties. In seeking to account for these discrepancies, we note several possible explanations including decomposition of acetylenedicarboxylic acid solutions since the authors were apparently unaware of this reaction nor were any special precautions noted. In addition we note some calculational practices which would introduce systematic errors. In the calculation of their thermodynamic pK_a^T from conditional pK_a's the correction term does not account for changes in ionic strength during the course of titration and the numerical constants in that term should be temperature dependent. We doubt, however, that these factors can cause errors large enough to account for the discrepancies. On the other hand, the attempt to correct for activity effects after calculating conditional pK_a values seems to indicate that these effects were not properly accounted for in calculating the hydrogen ion concentration. Apparently the authors have interpreted the measured pH values as $-\log [H^+]$ instead of $-\log a_{H^+}$. By so doing they consistently underestimated $[H^+]$ and this error then propagates to the other species concentrations through the conservation relationships. It should be noted that this underestimation of $[H^+]$ is inconsequential for much weaker acids, say, $pK_a > 5$. In such cases the correction term used by Bottei and Joern is adequate. In the present case, however, the initial solutions of H_2A (before any NaOH is added) are substantially dissociated so that underestimation of $[H^+]$ results in substantial errors in $[HA^-]$ and $[A^{2-}]$ as well. These solutions have analytical concentrations of $\simeq 0.01$ M H_2A and, if we assume $pK_{a1} = 0.7$ and $pK_{a2} = 2.3$, calculate $[H^+] = 0.0131$ M, $[H_2A] = 0.0003$ M, $[HA^-] = 0.0061$ M, $[A^{2-}] = 0.0035$ M, and $\gamma_{H^+} \simeq 0.90$. The measured pH of this solution is 1.93 $(= -\log \gamma_{H^+}[H^+])$, a value which the authors interpret as $[H^+] = 0.0117$ M. Consequently, the values of species concentrations, although not found explicitly in their calculations, are substantially at variance with the true concentrations giving rise to erroneous pK_a values. Another way to look at the problem is to note that undissociated H_2A comprises only 3% of the analytical H_2A. Once NaOH is added, the undissociated H_2A is even further reduced and rapidly becomes a negligible fraction of the total H_2A. However, pK_{a1} is effectively determined from this $[H_2A]$ as well as from $[HA^-]$ and $[H^+]$. Thus if $[H_2A]$ is almost nil and erroneous as well, the pK_{a1} value cannot be accurate. To the extent that pK_{a2} and pK_{a1} are interdependent, pK_{a2} value is suspect also.

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