

Protonation of Picolinic Acid: Determination of pK° , ΔH° , and ΔS°

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Using pH potentiometric measurements, concentration quotient and thermodynamic acid dissociation constants were determined for the dissociation of 2-pyridinium carboxylic acid. The determinations were carried out in aqueous media at five temperatures ranging from 20 °C to 55 °C and at two ionic strengths ($I = 0.10 \text{ mol dm}^{-3}$ and $I = 0.25 \text{ mol dm}^{-3}$). Standard enthalpies and entropies of the dissociation reaction were also obtained. At 25 °C, the thermodynamic values of these properties are $pK^\circ = 0.840 \pm 0.006$, $\Delta H^\circ = (-0.68 \pm 0.23) \text{ kJ mol}^{-1}$, and $\Delta S^\circ = (-18.4 \pm 0.8) \text{ J mol}^{-1} \text{ K}^{-1}$.

Picolinic acid (2-pyridine carboxylic acid, here referred to as P) is partially protonated in moderately acid aqueous media to form HP^+ . Green and Tong determined the value of pK for the dissociation of HP^+ to be 1.01 at 22 °C in aqueous solutions whose ionic strengths ranged from 0 to approximately 0.1 mol dm^{-3} (Green and Tong, 1956). Other authors have reported pK values of 1.03 at 25 °C in $0.10 \text{ mol dm}^{-3} \text{ NaClO}_4$ (Eberle and Robel, 1970), 0.92 at 25 °C in $0.20 \text{ mol dm}^{-3} \text{ NaNO}_3$ (Petitfaux et al., 1970), and 0.882 at 25 °C in $0.15 \text{ mol dm}^{-3} \text{ KNO}_3$ (Jons and Johansen, 1988). The value, $pK = 1.01$, obtained by Green and Tong is reported in the *Critical Stability Constants of Metal Complexes Database* (Smith and Martell, 1997). This value for the pK was used in an analysis of thermometric titration data to obtain $\Delta H^\circ = 2.2 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -12.1 \text{ J mol}^{-1} \text{ K}^{-1}$ at 25 °C in solutions whose ionic strengths ranged from 0.13 mol dm^{-3} to 0.27 mol dm^{-3} (Christensen et al., 1969). These estimates of the enthalpy and entropy appear to be the most accurate currently available.

The various estimates of the equilibrium dissociation constant mentioned in the previous paragraph are all based on the concentrations of the various species in solution rather than on their activities. We will refer to these constants as "concentration quotients" and denote them by K' . The thermodynamic equilibrium constants, obtained using activities, will be denoted by K° .

In order to investigate the dissociation properties and the structure of a moderately strong acid like the protonated species HP^+ , accurate estimates of both pK° , the thermodynamic constant, and its uncertainty as a function of temperature are required. Unfortunately, not all of this information is available in the literature. In this work, we use potentiometric methods to obtain values of pK° , ΔH° , and ΔS° and their uncertainties for the dissociation of HP^+ .

Experimental Section

Materials. All materials were of reagent grade. Samples of picolinic acid were obtained from the Aldrich Chemical Company and were used without further purification. Commercial HCl and NaOH were restandardized using customary titrimetric methods. Stock solutions containing weighed portions of picolinic acid and the appropriate amounts of KCl were assayed by alkimetric titrations. The purity of the picolinic acid was found to be $(99.5 \pm 0.1)\%$.

Procedures. Experiments involved the addition of either 0.1 mol dm^{-3} or 0.25 mol dm^{-3} HCl to a covered

thermostated cell equipped with conventional glass and calomel reference electrodes. Experiments were performed at (20, 25, 35, 45, and 55) °C. In each experiment, the temperature was monitored continuously and maintained to within ± 0.1 °C of the set point during a 1–2 h equilibration period before the calibration of the Beckman model 71 pH meter. Portions of a 0.75 mol dm^{-3} solution of P containing 0.1 mol dm^{-3} KCl were added to each cell containing 0.1 mol dm^{-3} HCl; portions of a mixture containing 0.75 mol dm^{-3} and 0.25 mol dm^{-3} KCl were added to each cell containing 0.25 mol dm^{-3} HCl. In this way the ionic strength of each titration mixture was maintained at the fixed value of either 0.1 mol dm^{-3} or 0.25 mol dm^{-3} . The volumes of the picolinic acid solutions were chosen so that the molar ratio of P to HCl ranged from 0 to 1.5. The pH of the solutions were recorded after equilibration periods of 15 to 30 min. Approximately 10 to 12 data points (pH vs volume of picolinic acid solution added) were obtained in each of the 10 experiments (titrations of solutions of ionic strength 0.1 mol dm^{-3} and 0.25 mol dm^{-3} at each of five temperatures). For the $I = 0.1 \text{ mol dm}^{-3}$ experiments, the values of pH ranged from 1.0 to 1.4; for the $I = 0.25 \text{ mol dm}^{-3}$ experiments, the corresponding range was 0.6 to 1.2.

Additionally, we confirmed the linear response of the pH meter for the KCl/HCl mixtures encountered in the titrations. Experiments involved "titrations" of 0.1 mol dm^{-3} HCl solutions with 0.1 mol dm^{-3} KCl solutions and of 0.25 mol dm^{-3} HCl with 0.25 mol dm^{-3} KCl. These experiments encompassed essentially the same range of pH as in the experiments designed to determine the picolinic acid protonation constants. In every HCl/KCl experiment, the differences between the calculated and observed values of the pH appeared to be randomly scattered. The root-mean-square (rms) values of these differences fell between 0.001 and 0.002 pH units. Excursions of individual differences seldom exceeded ± 0.003 pH units. These observations led us to conclude that the electrode response under the conditions of our experiments is essentially linear. It appears that minor variations of the junction potential at the reference electrode/solution interface and the possible effect of specific ion interactions play an insignificant role in the present experiments.

At the completion of each titration experiment, we confirmed the meter calibration with a fresh portion of the

Table 1. Concentration Quotients K' and Thermodynamic Acidic Dissociation Constants of HP^+ at Various Temperatures^a

	$t/^\circ\text{C}$				
	20.0	25.0	35.0	45.0	55.0
K' ($I = 0.10 \text{ mol dm}^{-3}$)	0.140	0.138	0.138	0.134	0.136
$\chi^2/\text{d.f.}$	0.1	0.1	0.2	0.4	0.1
K' ($I = 0.25 \text{ mol dm}^{-3}$)	0.138	0.138	0.137	0.137	0.132
$\chi^2/\text{d.f.}$	0.9	0.6	1.0	0.6	0.4
K° (from $I = 0.10 \text{ mol dm}^{-3}$)	0.145	0.143	0.143	0.140	0.142
($\text{p}K^\circ$)	0.839	0.845	0.845	0.854	0.848
K° (from $I = 0.25 \text{ mol dm}^{-3}$)	0.146	0.146	0.145	0.145	0.140
($\text{p}K^\circ$)	0.836	0.836	0.839	0.839	0.854

^a The standard errors in K and in $\text{p}K$ are ± 0.002 and ± 0.006 , respectively.

HCl solution. Deviations were generally less than ± 0.002 pH units and did not exceed ± 0.003 pH units.

Data Analysis and Results

The experiments provide sets of pH vs composition data at five different temperatures under conditions of constant ionic strength (either 0.1 mol dm^{-3} or 0.25 mol dm^{-3}). We determine the concentration quotient K' for HP^+ from this data using the following relations:

$$v c_p = [\text{HP}^+](V + v)R + [\text{P}](V + v)R \quad (1)$$

$$V c_{\text{HCl}} = [\text{H}^+](V + v)R + [\text{HP}^+](V + v)R \quad (2)$$

$$K' = [\text{H}^+][\text{P}]/[\text{HP}^+] \quad (3)$$

$$\text{pH} = -\log[\text{H}^+] = \text{pH}(\text{observed}) - \Delta \quad (4)$$

In these equations v and c_p are the volume and the analytical concentration of P in the picolinic acid solution; V and c_{HCl} are the initial volume and analytical concentration of the HCl solution. We assume that the solution volumes are additive. The factor R , the ratio of the density of water at 25°C to the density of water at the cell temperature, corrects for the thermal expansion of the mixture. The anionic picolinic acid species and the hydroxide ions are omitted because their concentrations are negligible in the solutions used in this work. The factor Δ is a meter calibration constant.

Optimized values of K' and Δ are obtained by applying a nonlinear regression analysis to the data using eqs 1–4 to formulate the model equation. The Levenberg–Marquardt algorithm (Press et al., 1992) was used to minimize χ^2 :

$$\chi^2 = \sum [(\text{pH}(\text{observed}) - \Delta) - \text{pH}(\text{calculated})]^2 / \sigma^2 \quad (5)$$

In this equation, $\text{pH}(\text{observed})$ denotes the experimental pH value, $\text{pH}(\text{calculated})$ is the calculated value obtained from the estimate of K' and Δ using eqs 1–4, and σ denotes the standard deviation of the pH readings. We set σ equal to 0.002 pH units.

Values of the concentration quotient constant K' and their uncertainties at each ionic strength and at each temperature are given in Table 1. The uncertainties, expressed as standard errors, were derived using propagation of variance based on $\sigma = 0.002$. The values of these uncertainties were all within 10–20% of 0.002 (approximately $\pm 1.5\%$ of K'). We confirmed these results by means

Table 2. Concentration Quotient and Thermodynamic Enthalpies and Entropies of HP^+ Dissociation

$\Delta H/\text{kJ mol}^{-1}$	-0.68 ± 0.23
$\Delta H/\text{kJ mol}^{-1}$ ($I = 0.10 \text{ mol dm}^{-3}$)	-0.74 ± 0.32
$\Delta H/\text{kJ mol}^{-1}$ ($I = 0.25 \text{ mol dm}^{-3}$)	-0.90 ± 0.34
$\Delta S^\circ/\text{J mol}^{-1} \text{ K}^{-1}$	-18.4 ± 0.8
$\Delta S/\text{J mol}^{-1} \text{ K}^{-1}$ ($I = 0.10 \text{ mol dm}^{-3}$)	-19.0 ± 1.0
$\Delta S/\text{J mol}^{-1} \text{ K}^{-1}$ ($I = 0.25 \text{ mol dm}^{-3}$)	-19.5 ± 1.1

of Monte Carlo simulations. The estimates of the uncertainties in K' using the two methods were essentially identical.

Table 1 also includes values of $\chi^2/\text{d.f.}$ (d.f. = degrees of freedom) for each regression. This quantity represents a goodness-of-fit estimator for each set of parameters. The values of χ^2 is obtained from the regression procedure; d.f. is equal to the difference between the number of data points and the number of adjustable parameters (in this case, 2). The values of $\chi^2/\text{d.f.}$ are in each case no greater than unity, indicating that the model provides an accurate representation of the chemical system.

We do not tabulate values of Δ , the meter calibration constant, since it is of no chemical interest. We do note that most of the values of Δ fell in the interval (-0.002 , $+0.002$) pH units and none exceeded 0.004 pH units. These results indicate that the estimate of $\sigma = 0.002$ for the uncertainty in pH is appropriate.

The thermodynamic dissociation constants, denoted by K° and $\text{p}K^\circ$, are also listed in Table 1. The values of K° differ from K' by the factor $\gamma_{\text{H}^+}\gamma_{\text{P}}/\gamma_{\text{HP}^+}$. Values of these activity coefficients were derived using the extended Debye–Hückel equation. In this equation, the A and B parameters were obtained from Robinson and Stokes (Robinson and Stokes, 1965). For the size of the H^+ ion, we use 0.9 nm , the value given in the literature (Kielland, 1937; Skoog et al., 1994). The size of the HP^+ ion was estimated to be 0.6 nm . The activity coefficient of the uncharged P species was set equal to 1. Because activity coefficients are not subject to random error, the statistical uncertainty in each value of K° (expressed here as the standard error of the mean) is essentially the same as the statistical uncertainty in the corresponding value of K' , namely, ± 0.002 . The uncertainty in $\text{p}K^\circ$ is then ± 0.006 .

The values of K° obtained from the two experiments carried out at different ionic strengths are essentially identical. For four of the five temperatures, the two values agree to within one standard error, while at 45°C , the two values differ by approximately two standard errors. Thus, at 25°C , our best estimate of $\text{p}K^\circ$ is the mean of the values calculated at the two ionic strengths: $\text{p}K^\circ = 0.840 \pm 0.006$.

Values of the enthalpies and entropies of dissociation were calculated using a van't Hoff analysis. In all cases, plots of $\ln(K)$ vs $1/T$ were linear with an apparently random scattering of points about the line. Because the uncertainties in the values of K are essentially identical to each other, an unweighted least-squares analysis could be used to obtain optimized values of the slope and intercept of the van't Hoff line.

Values of the enthalpies and entropies of dissociation together with their uncertainties (obtained from the rms scatter of the points about the regression line) are shown in Table 2. The scatter about each regression line was approximately equal to $0.01 \ln(K)$, a value consistent with the estimate of the uncertainty in the individual values of K° . The thermodynamic enthalpies and entropies are based on 10 data points, since the thermodynamic K° is the same for both ionic strengths. Each value of the enthalpy and of the entropy for the dissociation reaction

at a given ionic strength is based on five data points. At 25 °C, we find $\Delta H^\circ = (-0.68 \pm 0.23) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = (-18.4 \pm 0.8) \text{ J mol}^{-1} \text{ K}^{-1}$.

Error Analysis and Discussion

We next investigated the effects of systematic errors. These are three sources of systematic errors: (1) systematic errors in c_{HCl} , c_{P} , and V , (2) errors in the ionic activity coefficients γ_{H} and γ_{HP} , and (3) systematic errors in the pH vs v data.

Perturbations in the values of K for the first three error sources were evaluated by a recalculation procedure using independently adjusted values of c_{HCl} , c_{P} , and V as inputs to the regression analysis. Assuming a maximum excursion of 0.3% for each of these three sources, we find the contributions to the error in K to be 0.6, 0.1, and 0.4%, respectively. The contributions to the error in K° arising from errors in the two ionic activity coefficients were estimated by adjusting the ion-size parameter in the Debye–Huckel equation by 0.1 nm. These contributions were found to be approximately 2% for each ion.

Systematic errors in the pH data arise from two sources: (1) the possibility of non-Nernstian electrode response and (2) an offset error related to the calibration procedure. The first source was shown to be negligible by means of the calibration experiments. The second source was eliminated by using the meter offset parameter Δ in the regression procedure.

The results of this analysis indicate that the maximum likely excursion in the values of K , the concentration quotient, is less than 0.002, while excursions in K° , the thermodynamic constant, might be as large as 0.008. The increased uncertainty in K° results from the significant uncertainties in the activity coefficients. The effect of systematic errors on the calculated enthalpies was found to be negligible, and the effects on the entropies ΔS and ΔS° were only $0.1 \text{ J K}^{-1} \text{ mol}^{-1}$ and $0.4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. We observe that the effects of systematic errors on the concentration quotients and equilibrium constants is of the same order of magnitude as the uncertainties resulting from the random fluctuations in the pH readings, while these systematic errors have relatively little effect on the enthalpies and entropies.

Previous estimates of K at ionic strengths 0.10 mol dm^{-3} , 0.15 mol dm^{-3} , and 0.20 mol dm^{-3} are 0.093 (Eberle and Robel, 1970), 0.131 (Jons and Johansen, 1988), and 0.12 (Petitfaux et al., 1970), respectively. We find a value of 0.138 at 25 °C at both ionic strength 0.10 mol dm^{-3} and 0.25 mol dm^{-3} . Taking into account our estimate of ± 0.002 for the systematic error and ± 0.002 for the statistical

uncertainty, the present estimate of K is in reasonably good agreement with the value of 0.131 obtained at an ionic strength of 0.15.

In contrast to the values for K , the values for the thermodynamic enthalpies and entropies reported in this work ($\Delta H^\circ = -0.68 \pm 0.23 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -18.4 \pm 0.8 \text{ J mol}^{-1} \text{ K}^{-1}$) are significantly different from the previous values of $2.2 \pm 0.3 \text{ kJ mol}^{-1}$ and $-12.1 \text{ J mol}^{-1} \text{ K}^{-1}$ (no uncertainty provided) obtained from thermometric titrations (Christensen et al., 1969). This discrepancy is not unexpected, since the previously obtained values were derived from what is now known to be an inaccurate estimate of K . Although the thermometric titration method can provide highly accurate values of the enthalpies, these values are dependent on the extent of completion of the reaction and, thus, on the estimate of K .

Estimates of K° , ΔH° , and ΔS° have been employed both directly and indirectly via the interpretation of spectral data to estimate the partitioning of P between its molecular and zwitterionic forms (Green and Tong, 1956). Assuming that our estimates of these thermodynamic properties are more accurate than the previous ones, it would seem prudent to reexamine some of the results based on the values of these properties.

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