THERMODYNAMICS OF THE DISSOCIATION OF THE PYRIDINIUM ION

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Summary

The pK of the pyridinium ion at ionic strength 10^{-4} has been measured spectrophotometrically at ten temperatures in the range 5-50°C. At 25°C the enthalpy of dissociation, ΔH^0, is 4.28 ± 0.04 kcal mole^{-1}; and the entropy of dissociation, ΔS^0, is −9.6 ± 0.13 cal deg^{-1} mole^{-1}.

INTRODUCTION

In an investigation recently begun into the thermodynamics of multidentate ligands derived from pyridine, interpretation of our measurements called for comparison with similar information about simpler pyridine derivatives. Such information, even for pyridine itself, is sparse and discordant. From measurements of the dissociation constant of the pyridinium ion at 5.4°, 20°, and 35°, Essery and Schofield derived values of ΔH^0 4.37 ± 0.17 kcal mole^{-1} and ΔS^0 −9.2 ± 0.6 cal deg^{-1} mole^{-1}. By calorimetry at 25°, Mortimer and Laidler arrived at the values ΔH^0 5.7 ± 0.3 and ΔS^0 −4.76. The present paper reports a more extensive set of measurements of pK of the pyridinium ion, carried out with the object of fixing the thermodynamic quantities more certainly.

EXPERIMENTAL

Dissociation constants in dilute aqueous solution were determined by ultraviolet spectrophotometry from the expression

\[ K = \frac{a_H (E_{HA} - E)}{\gamma (E - E_A)} \]  

where E is the observed molar extinction coefficient; E_{HA} the molar extinction coefficient of the pyridinium ion; E_A the molar extinction coefficient of the conjugate base; and γ the activity coefficient of the pyridinium ion.

Methods of temperature control and of optical density and pH measurement have been described previously. In this work N.P.L. standard thermometers were used, and temperatures of the test solutions were constant and accurate to within ±0.03°C. The pH-meter was calibrated hourly against 0.05M potassium hydrogen phthalate (pH near 4.0) and a solution of 0.025M KH_2PO_4 and 0.025M Na_2HPO_4 (pH near 6.8). The meter was read to 0.001 pH units, and the relation pH = −log a_H was assumed to hold in this range.

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Pyridine for ultraviolet spectroscopy was used as supplied by Fluka. Gas chromatography indicated the presence of a single impurity to the extent of less than 0.3%; mass spectrometry showed the impurity to be a chloropyridine. This small proportion of a pyridine derivative is not expected to affect the validity of the results reported below.

Solutions in previously boiled water, cooled under nitrogen, were prepared by direct weighing followed by two successive dilutions in standardized volumetric apparatus, the final volume being adjusted at the temperature of the thermostat. $E_{HA}$ was determined from $1.5 \times 10^{-4}$ solutions, $10^{-2}$ in perchloric acid; $E_A$ from $2 \times 10^{-4}$ solutions, $10^{-3}$ in sodium hydroxide. Intermediate solutions were $2 \times 10^{-4}$ and were adjusted to pH values in the range pK $\pm 0.15$ by the addition of perchloric acid. Appropriate blank and cell corrections were applied to the observed optical densities. All solutions for a given temperature were made by diluting a single stock solution, so that small errors in its concentration, resulting from uncertainties in weighing a volatile hygroscopic liquid, could have no effect on the determination of pK.

![Absorption spectrum of (a) pyridine in dilute alkaline solution; (b) pyridinium ion. A, at 5°; B, at 50°.](image)

**RESULTS**

The absorption spectrum of aqueous pyridine is noticeably affected by temperature. Figures 1(a) and 1(b) respectively show the spectra of pyridine and the pyridinium ion on different scales, each at 5° and 50°. As the solutions were prepared at the temperature of measurement, the spectra are directly comparable in terms of molar absorbances. It will be observed that the degree of detail in the spectra diminishes with increasing temperature.
DISSOCIATION OF THE PYRIDINIUM ION

For the purposes of equation (1), the most accurate values of \( pK \) are obtained when \( E \) changes rapidly with pH but only slowly with wavelength. At each temperature, measurements were made at each of five intermediate pH values at three wavelengths chosen to meet this requirement in the range 250–258 \( \mu \).

**Table 1**

Dissociation Constants of the Pyridinium Ion

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( pK_{obs} )</th>
<th>( pK_{calc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°</td>
<td>5.422</td>
<td>5.422</td>
</tr>
<tr>
<td>10°</td>
<td>5.374</td>
<td>5.376</td>
</tr>
<tr>
<td>15°</td>
<td>5.322</td>
<td>5.329</td>
</tr>
<tr>
<td>20°</td>
<td>5.275</td>
<td>5.279</td>
</tr>
<tr>
<td>25°</td>
<td>5.229</td>
<td>5.229</td>
</tr>
<tr>
<td>30°</td>
<td>5.183</td>
<td>5.174</td>
</tr>
<tr>
<td>35°</td>
<td>5.123</td>
<td>5.119</td>
</tr>
<tr>
<td>40°</td>
<td>5.065</td>
<td>5.062</td>
</tr>
<tr>
<td>45°</td>
<td>5.003</td>
<td>5.003</td>
</tr>
<tr>
<td>50°</td>
<td>4.943</td>
<td>4.943</td>
</tr>
</tbody>
</table>

At pH values near \( pK \), the ionic strength was approximately \( 10^{-4} \), so that a simple Debye–Hückel correction gives \( \log \gamma \) as \(-0.005\). The constants in Table 1 have been calculated with this correction. Each represents a mean for five solutions, with a standard error of \( 0.004 \). They are in close agreement with Essery and Schofield's values: \( 5.4^\circ \), \( pK \ 5.44; \ 20^\circ \), \( 5.28; \ 35^\circ \), \( 5.11 \).

A plot of \( pK \) against \( 1/T \) is slightly curved. When the equations

\[
pK = A_1/T - A_2 \tag{2}
\]

and

\[
pK = A_1/T - A_2 + A_3T \tag{3}
\]

were fitted to the 50 experimental points, the variance about the regression line was significantly less for equation (3). Table 2 shows the computed values of the coefficients, together with

\[
\Delta H^0 = 2.303R(A_1 - A_3T^2)
\]

\[
\Delta S^0 = 2.303R(A_2 - 2A_3T)
\]

**Table 2**

Derived Thermodynamic Quantities

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( \Delta H^0 )</th>
<th>S.E.</th>
<th>( \Delta S^0 )</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°</td>
<td>2.13</td>
<td></td>
<td>-13.6</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.28</td>
<td>0.04</td>
<td>-9.6</td>
<td>0.13</td>
</tr>
<tr>
<td>50</td>
<td>5.83</td>
<td></td>
<td>-4.6</td>
<td></td>
</tr>
</tbody>
</table>

The standard errors of the thermodynamic quantities were derived in the course of the regression analysis.\(^7\) The calculated \( pK \) values in Table 1 were computed from equation (3) and the constants of Table 2.

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\(^7\) Davies, O. L., "Statistical Methods in Research and Production." 3rd Edn, p. 208. (Oliver and Boyd: London 1961.)