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°. At 25° the enthalpy of dissociation, ΔH^0 , is $4 \cdot 28 \pm 0 \cdot 04$ kcal mole⁻¹; and the entropy of dissociation, ΔS^0 , is $-9 \cdot 6 \pm 0 \cdot 13$ cal deg⁻¹ mole⁻¹.

INTRODUCTION

In an investigation recently begun¹ 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 $5 \cdot 4^{\circ}$, 20° , and 35° , Essery and Schofield² derived values of $\Delta H^0 \ 4 \cdot 37 \pm 0 \cdot 17$ keal mole⁻¹ and $\Delta S^0 \ -9 \cdot 2 \pm 0 \cdot 6$ cal deg⁻¹ mole⁻¹. By calorimetry at 25° , Mortimer and Laidler³ arrived at the values $\Delta H^0 \ 5 \cdot 7 \pm 0 \cdot 3$ and $\Delta S^0 \ -4 \cdot 76$. 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

$$K = \frac{a_{\rm H}(E_{\rm HA} - E)}{\gamma(E - E_{\rm A})} \tag{1}$$

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.¹ In this work N.P.L. standard thermometers were used, and temperatures of the test solutions were constant and accurate to within $\pm 0.03^{\circ}$. The pH-meter was calibrated hourly against 0.05 M potassium hydrogen phthalate (pH near $4.0)^4$ and a solution of 0.025 M KH₂PO₄ and 0.025 M Na₂HPO₄ (pH near 6.8).⁴ The meter was read to 0.001 pH units, and the relation pH = $-\log a_{\text{H}}$ was assumed to hold in this range.⁵

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¹ Green, R. W., and Goodwin, W. G., Aust. J. Chem., 1968, 21, 1165.

- ² Essery, J. M., and Schofield, K., J. chem. Soc., 1961, 3939.
- ³ Mortimer, C. T., and Laidler, K. J., Trans. Faraday Soc., 1959, 55, 1731.
- ⁴ Bower, V. E., and Bates, R. G., J. Res. natn. Bur. Stand., 1957, 59, 261.
- ⁵ Bower, V. E., and Bates, R. G., J. Res. natn. Bur. Stand., 1955, 55, 197.

Aust. J. Chem., 1969, 22, 721-3

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. $E_{\rm HA}$ was determined from 1.5×10^{-4} M solutions, 10^{-2} M in perchloric acid; $E_{\rm A}$ from 2×10^{-4} M solutions, 10^{-3} M in sodium hydroxide. Intermediate solutions were 2×10^{-4} M and were adjusted to pH values in the range pK ± 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.



Fig. 1.—Absorption spectrum of (a) pyridine in dilute alkaline solution; (b) pyridinium ion. A, at 5° ; B, at 50° .

RESULTS

The absorption spectrum of aqueous pyridine is noticeably affected by temperature. Figures l(a) and l(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.

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 m μ .

TABLE 1 DISSOCIATION CONSTANTS OF THE PYRIDINIUM ION pK_{calc} is derived from equation (3) and the parameters of Table 2

Temp.	5°	10°	15°	20°	25°	3 0°	35°	40°	45°	50°	
$\mathrm{p}K_{\mathrm{obs}}$	$5 \cdot 42_6$	$5 \cdot 37_4$	$5 \cdot 32_2$	$5 \cdot 27_{8}$	$5 \cdot 22_{9}$	$5 \cdot 18_{6}$	$5 \cdot 12_{3}$	$5 \cdot 06_{5}$	$5 \cdot 00_{3}$	$4 \cdot 94_{0}$	
$\mathrm{p}K_{\mathtt{calc}}$	$5 \cdot 422$	$5 \cdot 376$	$5 \cdot 329$	$5 \cdot 279$	$5 \cdot 229$	$5 \cdot 174$	$5 \cdot 119$	$5 \cdot 062$	$5 \cdot 003$	$4 \cdot 943$	

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° , pK 5.44; 20° , 5.28; 35° , 5.11.

A plot of pK against 1/T is slightly curved. When the equations⁶

$$\mathbf{p}K = A_1/T - A_2 \tag{2}$$

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

$$\Delta H^{0} = 2 \cdot 303 \mathbf{R} (A_{1} - A_{3} T^{2})$$

$$\Delta S^{0} = 2 \cdot 303 \mathbf{R} (A_{2} - 2A_{3} T)$$

TABLE	2
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DERIVED THERMODYNAMIC QUANTITIES A_1 , $-1 \cdot 00485 \times 10^3$; A_2 , $-15 \cdot 1042$; A_3 , $-2 \cdot 1822 \times 10^{-2}$ ΔH^0 in kcal mole⁻¹; ΔS^0 in cal deg⁻¹ mole⁻¹; S.E., standard error

Temp.	ΔH^0	S.E.	ΔS^0	S.E.	
5° 25	$3 \cdot 13$ $4 \cdot 28$	0.04	-13.6 - 9.6	0.13	,
50	5.83		-4.6		

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.

- ⁶ Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions." 2nd Edn, p. 517. (Butterworths: London 1959.)
- ⁷ Davies, O. L., "Statistical Methods in Research and Production." 3rd Edn, p. 208. (Oliver and Boyd: London 1961.)