ACID DISSOCIATION CONSTANTS OF PYRIDINE-2-ALDEHYDE AND PYRIDINE-2-ALDOXIME

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The acid dissociation constants of pyridine-2-aldehyde and its oxime have been measured spectrophotometrically at ionic strengths less than 0.001 in the temperature range 5–60°. Enthalpy and entropy changes associated with the equilibria are reported.

As a preliminary to investigating the complexing powers of pyridine-2-aldehyde and its oxime, a careful determination of their acid–base equilibria was necessary. Ultraviolet spectrophotometry is particularly well suited to this task since pyridine derivatives absorb strongly in two bands near 230 and 280 mμ with an intensity which depends on the degree of protonation of the ring nitrogen.[1] A second strong change in absorption accompanies dissociation of the oxime hydrogen. The high extinction coefficients make it possible to work with solutions more dilute than 10^{-3} M, where activity effects are almost negligible and easily calculated.

Experimental

Pyridine-2-aldehyde, supplied by L. Light and Co., after distillation under reduced pressure (25° (1 mm.)) was a colorless liquid (n^{20}D 1.5382) which became dark brown on prolonged exposure to air. When stored in the dark under nitrogen at 10° it showed no change in one year.

Pyridine-2-aldoxime, also from L. Light and Co., was recrystallized as colorless needles from hot water and dried *in vacuo* at room temperature. Its m.p. (113°) agreed with that reported by Lénhárt.[2]

Stock solutions of both substances were prepared in boiled distilled water, stored in the dark under nitrogen and renewed every three days. Solutions for spectrophotometry were prepared by dilution in glass apparatus rendered water-repellent by treatment with dichlorodimethylsilane and then re-calibrated. Small amounts of sodium hydroxide or perchloric acid were added to adjust the pH.

Measurements of pH were made with a Radiometer 4 pH meter standardized against 0.05 M potassium hydrogen phthalate and 0.01 M borax[3] at the temperature of the experiment. Solutions were tested in a thermostated cell within a grounded Faraday cage attached to the pH meter. Agreement between the two buffer solutions and reproducibility of pH measurements generally were found to be better than 0.01 pH unit.

Simultaneously with the pH measurement, a portion of the same solution was placed in a thermostated 1-cm. silica cell and its optical density at a suitable wave length was measured with a Hilger Uvispek Spectrophotometer. When observations were made below room temperature, a stream of dry nitrogen at the same temperature was passed through the cell compartment to prevent condensation of moisture on the optical faces.

Results

In 0.1 M perchloric acid solution, both pyridine-2-aldehyde and its oxime are present entirely in the cationic form, with the ring nitrogen protonated; and at pH 6–7 both exist exclusively as the uncharged species. At higher pH the oxime hydrogen begins to be titrated and the oxime is wholly anionic at pH 12, but the two equilibria do not over-

lap. It was therefore possible to prepare solutions containing any one species alone, and their absorption spectra at 25° are shown in Figs. 1 and 2. The solutions were found to be stable for several hours over the pH and temperature ranges with which we were concerned. The molar extinctions of the single species varied slightly with temperature and, since the precision of the pK determinations was closely dependent on these quantities, they were measured at each temperature on several independently prepared solutions of different concentration.

To determine the acid dissociation constants, ten solutions of each substance were prepared with pH values in the range pK $\pm$ 0.5, and their optical densities were measured at 260 mμ for the aldehyde and 295 mμ for the oxime. This was done at several temperatures between 5 and 60°, and the pK was calculated from each observation by means of the equation

$$pK = pH - \log \frac{E_A - E_{obs}}{E_{obs} - E_B} - \log \frac{\gamma_B}{\gamma_A} \quad (1)$$

where E denotes molar extinction coefficient and the subscripts A and B refer to acidic and basic forms, respectively. Since the concentrations were all near 10^{-4} M and no neutral salt was introduced, the simple Güntelberg[4] formula can be applied to show that the activity correction to pK is less than 0.0005 and hence can be neglected here.

In Table I, pK_1 represents the acid dissociation of the pyridinium group and pK_2 the oxime group. The acid strengths of the pyridinium groups at 25° are of the expected order, since they are markedly

TABLE I

ACID DISSOCIATION CONSTANTS

Temp., °C.	Pyridine-2-aldehyde NH+ pK_1	Pyridine-2-aldoxime NH+ pK_1	NOH pK_2
5	4.13	3.88	10.25
15	4.00	3.70	10.21
25	3.84	3.56	10.17
30	3.76	3.51	10.13
40	3.57	3.42	10.08
50	3.42	3.39	10.00
60	3.25	3.38	9.91
Equation 2			
A	−4287	+ 26,970	−8786
C	−67.94	+148.38	−112.63
D	− 0.1208	+ 0.2489	− 0.1229

stronger than in the unsubstituted pyridinium ion (pK = 5.18)[5] but weaker than the same group when

(1) R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

(2) B. Lénhárt, *Ber.*, **47**, 809 (1914).

(3) V. E. Bowers and R. G. Bates, *J. Research Natl. Bur. Standards*, **59**, 261 (1957).

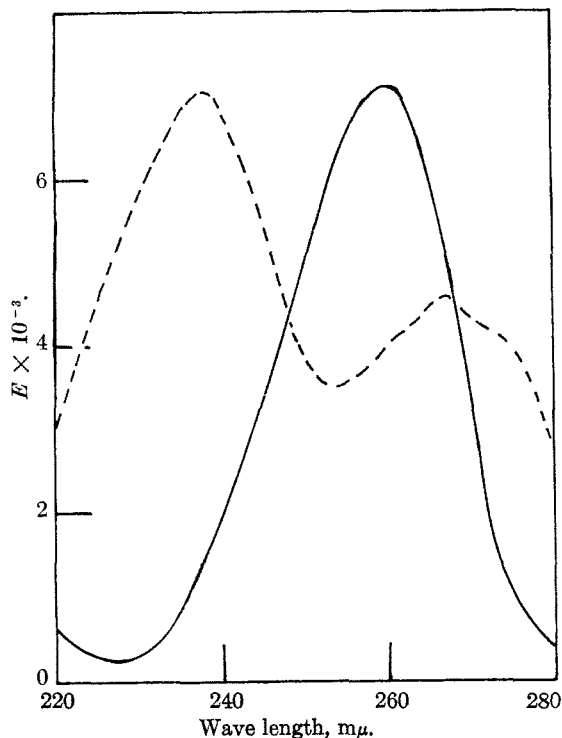(4) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

Fig. 1.—Absorption spectra of aqueous solutions of pyridine-2-aldehyde: continuous line, pH 1.6; broken line, pH 8.
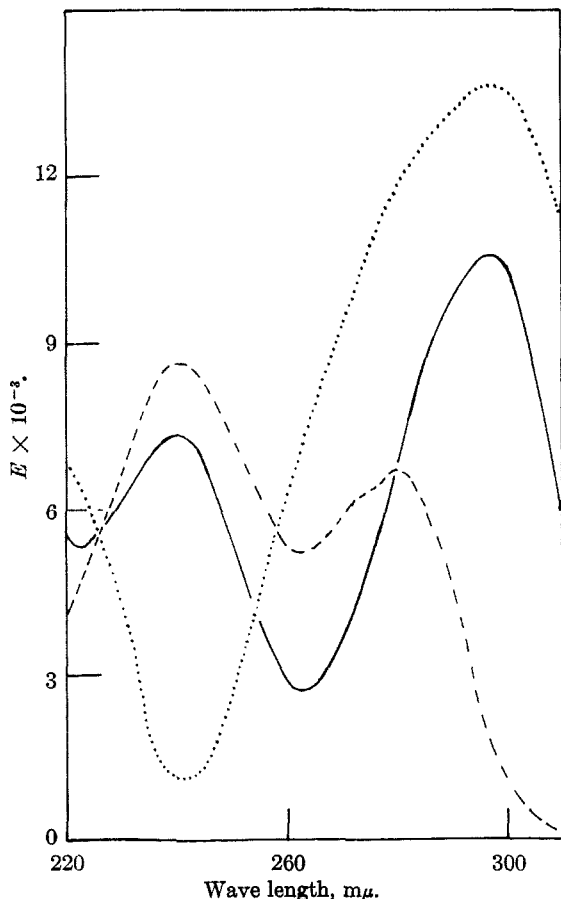

Fig. 2.—Absorption spectra of aqueous solutions of pyridine-2-aldoxime: continuous line, pH 1; broken line, pH 7; dotted line, pH 12.

there is an undissociated carboxyl radical in the 2-position ($pK = 2.21$).[1] The oxime dissociation is slightly stronger than in benzaldoxime ($pK = 10.7$),[6] as would be expected in view of the π-deficient nature of the pyridine ring.[7]

Since all measurements were made at pH values near the pK of the acid, the second term of eq. 1 was always quite small, so that the maximum error of an individual pK estimation should be little greater than that of the pH determination itself, namely, ± 0.01. The data of Table I, being the means of sets of ten observations, can be expected to have an even higher precision, which justifies their use in calculating enthalpies and entropies of dissociation.

We have followed the procedure of Harned and Robinson[8] and fitted the data of Table I to equations of the form

$$2.303R \log K = -A/T + C - DT \qquad (2)$$

The best values of the parameters A, C and D, obtained by the method of least squares, predict the experimental results with a mean deviation of 0.005. They are presented in Table I.

It follows from eq. 2 that

$$\Delta H^0 = A - DT^2$$

$$\Delta S^0 = C - 2DT$$

and calculated values of these quantities are reported in Table II.

TABLE II
THERMODYNAMIC FUNCTIONS

	Pyridine-2-aldehyde NH+		Pyridine-2-aldoxime NH+		NOH	
Temp., °C.	ΔH^0, kcal./ mole	ΔS^0, e.u.	ΔH^0, kcal./ mole	ΔS^0, e.u.	ΔH^0, kcal./ mole	ΔS^0, e.u.
5	5.1	− 0.7	7.7	9.9	0.7	−44.3
15	5.7	+ 1.7	6.3	4.9	1.4	−41.8
25	6.5	4.1	4.8	0.0	2.1	−39.3
30	6.8	5.3	4.1	− 2.5	2.5	−38.1
40	7.6	7.7	2.6	− 7.5	3.3	−35.7
50	8.3	10.1	1.0	−12.5	4.0	−33.2
60	9.1	12.6	−0.7	−17.5	4.9	−30.7

Equation 2 implies that, at a temperature $T_m = \sqrt{A/D}$, pK passes through a maximum or minimum according to whether A is negative or positive. At the same temperature $\Delta H^0 = 0$. Reference to a compilation of relevant data[9] reveals that A is nearly always positive; and it is well known that pK for many common carboxylic acids exhibits a minimum near room temperature. The first dissociation of pyridine-2-aldoxime also follows this general pattern, with a pK minimum within the experimental temperature range at about 56°. However, the other two dissociations examined here have negative values of A, implying pK maxima. The predicted maximum for pyridine-2-aldehyde is so far outside the experimental range as to be

(5) R. K. Murmann and F. Basolo, *J. Am. Chem. Soc.*, **77**, 3484 (1955).

(6) O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, 1918 (1926).

(7) A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, Chapter 4.

(8) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1959, p. 517.

meaningless, but the oxime pK does appear to go through a maximum very near $0°$.

Finally, it may be pointed out that the ΔS^0 values are characteristic. Ionization of the pyridinium group presumably follows the equation

$$RNH^+ + H_2O \rightleftarrows RNH + H_3O^+$$
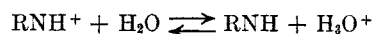
whose symmetry suggests that the entropy change should be small; but ionization of the oxime group is of the same kind as that of carboxylic acids, which usually is accompanied by a significant decrease of entropy.

THE HEAT OF FORMATION OF TITANIUM DIBORIDE: EXPERIMENTAL AND ANALYTICAL RESOLUTION OF LITERATURE CONFLICT

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Although the literature contains three independent values for the heat of formation of TiB_2 of ~ -70 kcal./mole, the present work shows that this agreement is fortuitous and that each value is in error for a different reason. Brewer and Haraldsen's value, -71.4 kcal., obtained from the reaction $TiN + 2BN = TiB_2 + 3/2\ N_2$, is questionable because of experimental difficulties and a mistake in the tabular data employed. Samsonov's experimental value, -70.04 kcal., obtained from the reaction $2TiO + B_4C = 2TiB_2 + CO_2$, is incorrect because of the use of unreliable thermodynamic data. Samsonov's calculated value, -73 kcal., obtained from an empirical relation between heat of formation and volume change, could not be duplicated. Another value for the heat, -32 kcal., obtained by Schissel and Williams with a mass spectrometer and Knudsen cell, is shown to be low by a stability comparison with TiC and B_4C. When corrected, within appropriate limits of error, the three experiments yield results in agreement with the recent calorimeter value of Lowell and Williams, -50 ± 5 kcal./mole.

I. Introduction

While investigating the vaporization of the refractory hard metal TiB_2 with a mass spectrometer, Schissel and the writer[1] obtained and reported a value of -32 kcal./mole for the heat of formation. This value differs substantially from the four other literature values, all of which are ~ -70 kcal./mole. By a study of the reaction of titanium and boron in a nitrogen atmosphere, Brewer and Haraldsen[2] obtained -71.4 kcal.; by a study of the reduction of TiO_2 by carbon and boron carbide, Samsonov[3] obtained -70.04 kcal.; by use of an empirical formula of Kubaschewski,[4] Samsonov[5] calculated -73 kcal.; and by analysis of the literature data Krestovnikov and Vendrikh[6] selected the value -70.00 kcal. In an attempt to reconcile the conflict, the writer performed several additional experiments and analyzed the papers mentioned.

The additional experiments were of three types: (1) stability comparisons in which bounds were placed on the unknown heat of formation by comparison with other compounds; (2) direct reaction of the elements in a high temperature calorimeter, with Lowell,[7] and (3) a refinement of the Brewer and Haraldsen experiment.[2] A discussion of each of these experiments follows as Section II. In Section III, an analysis of each of the earlier determinations of $\Delta H_f(TiB_2)$ is presented.

(1) P. O. Schissel and W. S. Williams, *Bull. Am. Phys. Soc. Ser. II,* **4**, No. 3 (1959).

(2) L. Brewer and H. Haraldsen, *J. Electrochem. Soc.,* **102**, 399 (1955).

(3) G. V. Samsonov, *Zhur. Priklad. Khim.,* **28**, 1018 (1955).

(4) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Third Ed., Pergamon Press, 1958.

(5) G. V. Samsonov, *Zhur. Fiz. Khim.,* **30**, 2057 (1956).

(6) A. N. Krestovnikov and M. S. Vendrikh, *Izvest. Vysshikh Ucheb. Zavednii Tsvet. Metall.,* No. 2, 54 (1959).

(7) C. E. Lowell and W. S. Williams, *Rev. Sci. Instr.,* in press.

II. Description of Present Work

(1) **Stability Comparisons.**—The results of the first stability comparison, presented in Table I, establish the coexistence of TiB_2 and C at temperatures up to $2250°$, in agreement with the ternary diagram presented by Brewer and Haraldsen.[2] Thus ΔF and $\Delta H > 0$ for the reaction $TiB_2 + 3/2\ C = TiC + 1/2\ B_4C$. From the heats of formation of B_4C and TiC,[4] $\Delta H_f(TiB_2) < -51 \pm 5$ kcal./mole. This result shows that the -32 value for $\Delta H_f(TiB_2)$ must be in error.

Other comparisons were made against various titanium and boron compounds, but because of a deficiency of thermodynamic data for these materials the results are principally of qualitative interest (Table II).

TABLE I
RESULTS OF INVESTIGATION OF THE REACTION
$TiB_2 + 3/2C = TiC + 1/2\ B_4C$

Reactants	Products	Crucible	Temp. (°C.)	Time (hr.)
$TiB_2 + C$	$TiB_2 + C$	TiB_2	1900	1.5
$TiB_2 + C$	$TiB_2 + C$	carbon	2250	8
$TiC + 2B$	$TiB_2 + C$	carbon	2050	4
$TiC + 2B$	$TiB_2 + C$	carbon	2100	3
$2TiC + B_4C$	$2TiB_2 + 3C$	carbon	2000	1

(2) **Direct Reaction Calorimeter.**—In the calorimeter used by Lowell and Williams,[7] titanium and boron powders were mixed in the correct ratio to yield TiB_2, packed in a thermally isolated graphite capsule and heated *in vacuo*. At a temperature of $1500°$ an exothermic reaction occurred, raising the temperature of the capsule above that of the heater by $1000°$ in 0.2 second. By X-ray diffraction analysis of a pulverized sample the product was shown to be all TiB_2. The temperature rise of the capsule was followed with a calibrated photo-