cific conductance increases linearly with temperature over the range studied.

The conductances of solutions of hydrogen fluoride in iodine pentafluoride also were studied and the results are summarized in Table IV. Both specific and molar conductances decrease at first, then increase, with increase in concentration. Molar conductances are very low in the rather high concentration range studied and hydrogen fluoride must be only slightly ionized in these solutions. The addition of hydrogen fluoride must lead to an actual decrease in the concentration of ionic species present for solutions with hydrogen fluoride concentration between 0.16 and 3.75 molar.

The temperature coefficient of conductance has also been measured at several concentrations (Table IV). The temperature coefficient is positive for each pure component but decreases to zero in a solution with mole fraction hydrogen fluoride about 0.6.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMERICAN UNIVERSITY OF BEIRUT]

The 2,2′,2″-Tripyridine System

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The thermodynamic acid dissociation constants for the diacid base 2,2′,2″-tripyridine are $pK_1 = 2.64 \pm 0.07$ for equation 1 and $pK_2 = 4.33 \pm 0.03$ for equation 2. The composite $pK_{1,2}$ is thus 7.0 ± 0.1. The ferrous complex has the formula $FeB_2H_2^{+4}$ and the equilibrium $pK_D = 20.4 \pm 0.2$. Kinetic studies confirm this formula and support the pK_D value in addition to indicating that the ferrous complex is formed through the free base with some form of the ferrous ion involved in the rate-determining step. The work was done at 22–23°.

Compounds containing the —N=C—C=N— linkage have been studied as chelating agents. In particular the complexes of iron(II) with 1,10-phenanthroline[1] and 2,2′-bipyridine[2] have been extensively studied.

2,2′,2″-Tripyridine has received comparatively little study. Brandt and Wright[3] found it to be a diacid base

$$BH_2^{++} \rightleftarrows BH^+ + H^+ \qquad (1)$$

$$BH^+ \rightleftarrows B + H^+ \qquad (2)$$

where B = 2,2′,2″-tripyridine. They were able, by potentiometric and conductometric methods, to find a composite $pK_{1,2}$ of 7.1 for the acid dissociation, but were unable to isolate the values for the separate steps. They also found the ferrous complex to contain 2 molecules of tripyridine to one of iron(II) and spectrophotometrically determined the instability constant obtaining an average value of 1×10^{-18}.

In this investigation the acid dissociation constants K_1 and K_2 are isolated, the nature of the ferrous complex elucidated and the kinetics studied for the formation and dissociation of the ferrous complex.

Experimental

Reagents.—2,2′,2″-Tripyridine was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. Stock solutions were prepared from the material that was recrystallized from a 40–60° b.p. cut of petroleum ether; m.p. 80–82°.

Stock solutions of iron(II) were prepared from reagent grade hydrated ferrous ammonium sulfate. A small amount of hydroxylamine hydrochloride was added to prevent oxidation.

Reagent grade hydrochloric acid, sodium acetate, sodium hydroxide and sodium mono basic phosphate were used in preparing buffer solutions. Since the latter interferes in the formation of the ferrous complex of the tripyridine[4] it was not used when iron was present.

Instruments.—All absorption measurements were made on a Beckman Model DU Spectrophotometer using matched one centimeter silica or Corex cells. All pH measurements were made on a Cambridge glass electrode pH meter.

Equilibria and Kinetic Studies.—For the formation of the ferrous complex a buffered solution of the tripyridine was prepared in a 50-ml. volumetric flask leaving just sufficient space for the aliquot of iron(II) stock solution. After the addition of the latter the reaction was followed spectrophotometrically until there was no further change in absorption. All solutions were allowed to stand at least 24 hours before measurements were taken for the equilibria studies.

For the studies of the dissociation of the ferrous complex a concentrated solution of the chelate was prepared at a high pH, where little dissociation occurs. Aliquots of this solution were diluted to a sufficiently low pH where considerable dissociation occurs. The dissociation was followed spectrophotometrically until equilibrium was established.

Conditions.—The temperature of all the studies was 22–23°. The final ionic strength of all solutions was 0.10 except in the case of several of the more acid solutions where it was slightly greater.

Results and Discussion

Acid Dissociation Constants.—Figure 1 shows the absorption curves for the various forms of the base. The BH_2^{++} form gave a molar extinction coefficient ϵ_{max} 2.18×10^4 at 288.5 mμ, $p\text{H} < 1.5$ and ϵ_{min} 1.44×10^4 at 281.0 mμ, pH 4.30. For BH^+, ϵ_{max} 1.74×10^4 at 321.5–323.0 mμ, $p\text{H} < 3.0$ and ϵ_{min} 0.60×10^4 at 313 mμ, $p\text{H} > 11.0$. The free tripyridine (B) showed ϵ_{max} 1.60×10^4 at 285 mμ, $p\text{H} > 5.5$.

Plotting total molar extinction coefficient *versus* pH resulted in the usual type curves showing the transition from one form to another.

Let K_2 be the thermodynamic dissociation constant for equation 2. It may be shown that

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(1) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

(2) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 57, 736 (1950).

(3) W. W. Brandt and J. P. Wright, THIS JOURNAL, **76**, 3082 (1954).

(4) M. L. Moss and M. G. Mellon, *Anal. Chem.*, **14**, 862 (1942).

$$pK_2 = p\text{H} + \log\frac{(\epsilon_X - \epsilon_B)}{(\epsilon_{BH^+} - \epsilon_X)} + \log\gamma_{BH^+}$$

where ϵ_X is the total molar extinction coefficient.

From Debye–Hückel theory $\log\gamma_{BH^+} = -(0.509)(1)\,I^{1/2}/(1 + I^{1/2})$. Similarly

$$pK_1 = p\text{H} + \log\frac{(\epsilon_X - \epsilon_{BH^+})}{(\epsilon_{BH_2^{++}} - \epsilon_X)} + \log\frac{\gamma_{BH_2^{++}}}{\gamma_{BH^+}}$$

The average values of pK_1 and pK_2 obtained from substitution in the above formulas are $pK_1 = 2.64 \pm 0.07$ and $pK_2 = 4.33 \pm 0.03$.

The composite $pK_{1,2}$ is 7.0 ± 0.1 which compares favorably with the value of 7.1 given by Brandt and Wright.[3] It is not possible to calculate the ionic strength correction from the data given in their paper, but such a correction would reduce their value. 2,2',2''-Tripyridine is thus seen to be a stronger base than other compounds having the —N=C—C=N— linkage.[1,2,5]

No irregularities in the spectra were observed in solutions containing as much as 60% H_2SO_4. In more concentrated solutions the peaks at 288.5 and 321.5 mμ became smaller, finally culminating in a new peak with $\epsilon = 2.75 \times 10^4$ at 309 mμ in 95% H_2SO_4. The peak observed could be due to the addition of a third proton to the tripyridine. It is not possible, however, to obtain any quantitative values for the dissociation constant. If the peak is due to the formation BH_3^{+3}, the pK will be negative.

The addition of a third proton would be expected to be difficult. If there is resonance across the internuclei bonds giving partial double bond character, the molecule is practically planar. In all three possible confirmations the addition of a third proton would be greatly hindered.

Ferrous Complex.—The ferrous complex exhibits a maximum at 552 mμ and shows three additional peaks in the ultraviolet region of 220–320 mμ. Only in the case of the peak in the visible region is the absorption not complicated by the absorption of the base forms of tripyridine. For this visible peak the absorption obeyed Beer's law. The extinction coefficient was found to be 1.16×10^4 by the use of solutions containing excess of tripyridine. Assume

$$FeB_2^{++} \rightleftarrows Fe^{++} + 2B$$

Then

$$K'_D = \frac{(Fe^{++})(B)^2}{(FeB_2^{++})} \qquad (3)$$

Let

$C_{Fe^{++}}$ = analytical concn. of iron(II)

C_B = analytical concn. of tripyridine (B)

Then

$$(Fe^{++}) = C_{Fe^{++}} - (FeB_2^{++})$$
$$(B) = C_B - 2(FeB_2^{++}) - (BH^+) - (BH_2^{++})$$

Substituting for the latter two terms the expression for the acid dissociation constants and rearranging

$$(B) = \frac{C_B - 2(FeB_2^{++})}{1 + \frac{(H^+)}{K_2} + \frac{(H^+)^2}{K_{1,2}}}$$

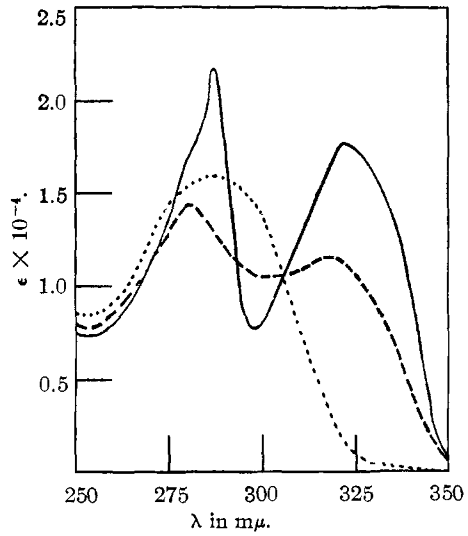

Fig. 1.—Molar extinction coefficient *versus* wave length in mμ for 2,2',2''-tripyridine: ——, pH 1.05; ------, pH 4.30; ...., pH 11.0.

Since

$$(FeB_2^{++}) = \frac{A}{\epsilon_{FeB_2^{++}}}$$

where A is the absorbance and $\epsilon_{FeB_2^{++}}$ the extinction coefficient for the complex, all the values necessary to compute K'_D by equation 3 are available. The values of K'_D thus obtained were found to be strongly pH dependent. This would explain the variation in the results of Brandt and Wright.[3]

pK'_D was found to vary linearly with pH. A new pK_D defined as $pK_D = pK'_D + 2p\text{H}$ was found to be independent of the acidity in the pH range 0.98–4.61. The average value of pK_D was 20.4 ± 0.2.

This implies that the formula of the complex is $FeB_2H_2^{+4}$ and the equilibrium is

$$FeB_2H_2^{+4} \rightleftarrows Fe^{++} + 2B + 2H^+$$
$$K_D = \frac{(Fe^{++})(B)^2(H^+)^2}{(FeB_2H_2^{+4})}$$

Investigators have previously postulated the existence of one proton in the bis-(1,10-phenanthroline)–iron(III) ion[1] and in the tris-(2,2-bipyridine)–iron(II) ion.[6] However, this is the first instance where there is strong support for a complex of this type containing hydrogen ion in solutions of low acidity. At a pH of 4.6 more than 60% of the tripyridine is in the free base form.

Brandt and Wright[3] plotted pK_D *versus* average basicity per nitrogen for several ferrous complexes of bases containing the —N=C—C=N— system. Only the points for the complexes of 2,2',2''-tripyridine and 2,2'-bipyridine were off the straight line that passed through the points of four other bases. The value of pK_D = 20.4 for tripyridine reported here if used in their plot would cause the tripyridine point to fall nearly on their straight line. Thus only the point for 2,2'-bipyridine is off the line.

Outside the pH range 0.98–4.61, reproducible results were not obtained, possibly indicating a

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[5] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 523–525.

[6] P. Krumholz, *Nature*, **163**, 725 (1949); *Anais Acad. Brasil. Chem.*, **22**, 263 (1950); *C. A.*, **45**, 3209 (1951).

transition in the nature of the complex. Unfortunately the upper *p*H is limited by the range of acetate buffers as the other available non-absorbing buffer reagent phosphate, interferes with the formation of the ferrous complex.[4]

The high value of ϵ for the ferrous complex makes tripyridine a contender as a chelating agent for the analytical determination of iron. However, the value of ϵ is not much greater than that of 1,10-phenanthroline. The latter has the advantage of being more easily purified and in being workable over a much larger range of *p*H. At $p\text{H} < 3.5$ the back reaction in the case of tripyridine is appreciable. The greater maxima in the ultraviolet are all complicated by absorption of non-complexed tripyridine.

An additional experiment performed on a solution 0.1 *M* in Fe^{++} and 1.2×10^{-4} *M* in tripyridine yielded a reduction in the apparent extinction coefficient of more than 50% at 552 mμ. Studies showed peaks at 274 and 319 mμ presumably due to the formation of a 1:1 complex.

Kinetic Studies.—The reaction rates for the formation and dissociation of the complex were followed spectrophotometrically.

$$\text{Fe}^{++} + 2\text{B} + 2\text{H}^+ \rightleftharpoons \text{FeB}_2\text{H}_2{}^{+4} \qquad (4)$$

$$+\, d(C_c)/dt = k_f(\text{Fe}^{++})(\text{B})^2(\text{H}^+)^2 - k_d(C_c) \qquad (5)$$

where C_c = concn. of complex. Since all solutions were buffered the (H^+) was constant during any given run. In the rate of formation studies the analytical concentration of the tripyridine was 10 times that of iron(II). This was found to be about the optimum ratio for a fairly constant base concentration and a convenient reaction time. It was necessary that the *p*H be less than 1.5, otherwise the reaction would reach equilibrium too quickly. Less than 0.01% of the tripyridine was in the form of the free base in this *p*H range. With (H^+) and (B) effectively constant (5) may be integrated to yield

$$-\ln (C_E - C_c) = \frac{k_f(C_{\text{Fe}^{++}})(\text{B})^2(\text{H}^+)^2}{C_E}\, t + \text{const.}$$

where C_E = concn. of complex at equilibrium. The plots of $\ln(C_E - C_c)$ yield straight lines. Utilizing the value for (B) as calculated from the acid dissociation constant k_f may be evaluated. The average value of $k_f = 6.5 \pm 1.3 \times 10^{15}$ (moles/liter)$^{-4}$ sec.$^{-1}$.

For the decomposition of the complex plots of $\ln(C_c - C_E)$ *versus* t yield straight lines. The average value of $k_d = 5.0 \pm 0.8 \times 10^{-5}$ sec.$^{-1}$.

The equilibrium constant $K_D = k_d/k_f = 7.7 \times 10^{-21}$. $pK_D = 20.1 \pm 0.2$ from the kinetic studies which compares favorably with the value of 20.4 ± 0.2 from the purely equilibrium study.

Since the equilibrium constants for the complex as determined by two independent methods are in agreement, some indication is given of the mechanism of formation of the complex. The formation of the complex is slower in the more acid solutions. Thus it is most likely that the formation of the complex proceeds through either B or BH^+. If the latter were the case the formation equation would be $\text{Fe}^{++} + 2\text{BH}^+ \rightleftharpoons \text{Fe B}_2\text{H}_2{}^{+4}$ and the corresponding formation constant k_f would be of the order of 10^{10} (moles/liter)$^{-4}$ sec.$^{-1}$. Were this the case, calculation of K_D from the rate constants would give a value of about 10^{-15}. This value is inconsistent with the value of K_D as determined from the equilibrium study. Thus the complex is formed through the free base as indicated in equation 4.

Experiments have shown that there is no measurable time lag in the attainment of the acid–base equilibria in equations 1 and 2 when no iron is present. Therefore the rate-determining step in the formation of the ferrous complex involves some form of the ferrous ion.

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