THE 2,2',2" TRIPYRIDINE SYSTEM

BY

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2,2',2" TRIPYRIDINE

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ABSTRACT

The base 2,2',2" tripyridine was investigated spectrophotometrically. Two acid-base equilibrium constants and the dissociation constant of its complex with ferrous ion were determined. The kinetics of the latter reaction was studied.

Tripyridine forms a diprotonic acid in solutions of low pH. The equilibrium constants determined were:

for $BH_2^{++} \rightleftharpoons BH^+ + H^+ \quad pK_1 = 2.64 \pm 0.07$

for $BH^+ \rightleftharpoons B + H^+ \quad pK_2 = 4.33 \pm 0.03$

The composite equilibrium constant, pK_a equals 7.0 ± 0.1. This compares favorably with Brandt's value of 7.1 (5).

With ferrous ion, tripyridine forms the complex $FeB_2H_2^{4+}$ in solutions buffered in the pH range 0.98 - 4.61.

$$Fe^{++} + 2B + 2H^+ \rightleftharpoons FeB_2H_2^{4+}$$

Spectrophotometric study of solutions at equilibrium gave $pK_D = 20.4 \pm 0.2$.

The reaction rates for the formation and dissociation of the ferrous tripyridine complex were followed spectrophotometrically.

$$Fe^{++} + 2B + 2H^+ \underset{k_d}{\overset{k_f}{\rightleftharpoons}} FeB_2H_2^{4+}$$

The rate of formation was determined in buffered solutions of low pH in the presence of excess tripyridine at pH = 1.17, k_f had the value $2.7 \times 10^{17}\ (M/l)^{-4}\ min.^{-1}$.

The dissociation of the complex was followed in buffered solutions of low pH. The dissociation rate complex k_d equaled 2.26×10^{-3} min.^{-1} at pH 1.27.

From the rate constants, the equilibrium constant was calculated. pK_D from reaction rates is 20.1 which is consistent with the value of 20.4 calculated from equilibrium data.

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INTRODUCTION

The purpose of this thesis is to describe the author's recent spectrophotometric investigation of the base 2,2',2" tripyridine, and its behavior as a chelate with ferrous ion.

Theoretical Aspects of Absorption Spectra.

Organic molecules will react with light energy of appropriate wavelength with the absorption of quanta of energy. The amount of this energy, E, may be expressed mathematically by the relation.

$$E = hc/\lambda$$

where h is Planck's constant, c is the velocity of light and λ is the wavelength. Thus the greater the amount of energy required, the shorter the wavelength.

This energy, E, is the amount of energy necessary to raise an electron from its ground state to its excited state. While the E value for a single atom is very specific, resulting in absorption of a single wavelength ; molecules in solution will absorb in a region or band with one wavelength at a maximum and a gradual falling off of absorption on each side. Increasing resonance in a molecule usually results in the absorption of longer wavelengths. This occurs because the difference in energy between the highest level π orbital in the ground state and the lowest possible excited state decreases as the number of conjugated double bonds increases. (6, 16)

Spectrophotometric Nomenclature and Laws.

Table I

Definition of Symbols

T_s	transmittancy.
A	absorbance.
I_o	intensity of light transmitted by pure solvent.
I	intensity of light transmitted by solvent plus absorbing material.
ϵ	molar extinction coefficient.
b	cell thickness in centimeters.
c	concentration in moles per liter.
λ	wavelength - here expressed in mμ.
mu	millimicron = 10^{-7} cm.

Absorption Laws

Bougerer's Law (Lambert's): When a ray of monochromatic light enters an absorbing medium, its intensity decreases exponentially with an increase in the thickness of the medium transversed.

$$A = \log 1/T_s = \log I_o/I = Kb$$

where K is a constant depending upon the wavelength, the nature of the medium and the concentration.

Beer's Law: The intensity of monochromatic light passing through a medium, decreases exponentially as the concentration of the absorbing material increases.

$$A = \log 1/T_s = \log I_o/I = Kc$$

where K is a constant dependant upon wavelength, the nature of the medium, and the thickness of the solution.

These two laws have been combined into the Beer-Bouger law:

$$A = Kcb$$

This can be rearranged:

$$K = A/cb = \epsilon$$

if b is one centimeter and c is the molar concentration, K is called the molar extinction coefficient. (18)

Historical:

2,2',2" tripyridine was first reported by Morgan and Burstall (12) in 1932. It appeared as one of twenty side products obtained in the production of 2,2' bipyridine by the dehydrogenation of anhydrous ferric chloride.

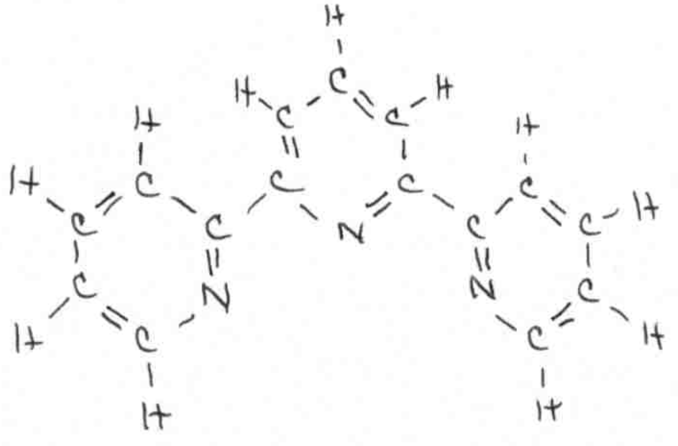

Fig. 1 2,2',2" tripyridine

The tripyridine* was characterized as giving a deep purple color in the presence of ferrous ions. This color also appeared in the easily obtained complex bromide: $Fe(tripy)_2Br_2.4H_2O$. (13)

This tripyridine was found to form stable chelates with many metals. It acted as a tridentate group, the complex containing one or two tripyridine molecules to each metal atom. The complex with ferrous ion was reported to have one ferrous ion to two molecules of tripyridine.(14)

Moss and Mellon (15), in their study of the iron-tripyridine system, reported the maximum optical density of the complex to occur at a wavelength (λ) of 552 millimicrons. They found that Beer's law held at this wavelength and reported the extinction coefficient (ϵ), per mole of ferrous ion, equal to 11,500. Also, they detected no change in intensity or hue over a pH range of 3 to 10. Recently, Pflaum and Brandt reported the extinction coefficient of this complex to be 12,500 at $\lambda = 552$. (17)

In 1954 Brandt and Wright (5) reported that potentiometric studies of the tripyridine acid-base equilibria gave a composite pK_a of 7.1 for the reactions:

$$\text{Tripy } H_2^{++} \rightleftharpoons \text{Tripy } H^+ + H^+$$

$$\text{Tripy } H^+ \rightleftharpoons \text{Tripy} + H^+$$

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* Throughout this paper tripyridine, tripy and B. will be used to designate 2,2',2" tripyridine.

where:

$$K_a = (\text{Tripy})(H^+)^2/(\text{Tripy } H_2^{++})^*$$

They also determined the Instability Constant for the iron (II) tripyridine ion spectrophotometrically, and reported $K_D = 1 \times 10^{-18}$.

Similar studies have been made on 2,2' bipyridine (2,15), 1,10 phenantholine (4,10,11) and its derivatives (4), and 2,2' biquinoline (11). Earlier studies of the acid-base equilibria of these compounds indicated that a monobasic acid was formed in solutions of low pH (2,4,10). However, recent work at this University showed that in solutions of negative pH, a second proton is added to the base. (11) In general, these compounds form bidentate complexes with ferrous ion, having the formula FeB_3^{++}.

A summary of equilibrium data for the complexes discussed will be found in Table II.

Various workers have studied the kinetics of the formation of iron chelates of compounds having the -N=C-C=N- linkage. Working independently Krumholtz (8) and Baxendale and George (3) determined the reaction for the formation of $Fe(Bipy)_3^{++}$ to be third order with respect to 2,2' bipyridine, first order with respect to iron and fourth order overall. Earlier, Krumholtz reported the rate for the

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[*] Throughout the paper ( ) will be used to denote concentration in moles per liter.

Table II

Chelate Dissociation Constants*

Compound	Metal ion	pK_d	Method	Ref.
2,2' bipyridine	H^+	4.334		2
		4.43		9
	Fe^{++}	$17.6(k_1k_2k_3)$	Beer's Law	1
		$17.4(k_1k_2k_3)$	Beer's Law	9
2,2'biquinoline	H^+	$-0.95(k_1)$	Beer's Law	11
		$2.68(k_2)$	Beer's Law	11
1,10 Phenanthroline	H^+	4.91	Potentiometric	10
		4.96	Potentiometric	12
		5.9	Beer's Law	7
		$-0.9(k_1)$	Beer's Law	11
		$5.46(k_2)$	Beer's Law	11
	Fe^{++}	$21.5(k_1k_2k_3)$	Reaction Rates	4
		$21.3(k_1k_2k_3)$	Potentiometric	4
		$21.3(k_1k_2k_3)$	Polarographic	10
2,2',2"tripyridine	H^+	$7.1(k_1k_2)$	Potentiometric	5
	Fe^{++}	$18\ (k_1k_2)$	Beer's Law	5

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* For additonal data on Dissociation constants of Chelates, the reader is referred to Martell, A.E. & Calvin, M., <u>Chemistry of the Metal Chelate Compounds</u>, 514 ff., Prentice Hall Inc., New York, 1952.

decomposition of the complex to be first order, having as the intermediate and rate determining step, the decomposition of $FeBipy_3H^{3+}$. (9) This intermediate, he found, occurred in both the formation and dissociation of the complex. (8)

The kinetics of the reactions of ferrous ion with orthophenanthroline and its derivatives have been studied with similar results. (4,10)

EXPERIMENTAL

Materials Used. 2,2',2" tripyridine was obtained from the G. Frederick Smith Chemical Company. It was recrystallized from a 40 - 60° Cut of petroleum ether. Stock solutions of the base were prepared by dissolving an accurately weighed amount (ca. 0.2 g) of the tripyridine in reagent grade hydrochloric acid and diluting to 500 ml. This resulted in a solution about 1.5×10^{-3} M. in the base and 1.0M in HCl.

Stock solutions of iron (II) were prepared from reagent grade hydrated ferrous ammonium sulfate and hydroxylamine hydrochloride yielding solutions about 3×10^{-3} M in Fe^{++} and 0.01 M in $NH_2OH.HCl$.

For use as buffers, stock solutions were prepared from reagent grade chemicals: hydrochloric acid, sodium acetate, sodium mono basic phosphate and sodium hydroxide.

Instruments. Absorptimetric data were obtained by use of a Beckman Model DU Spectrophotometer. Measurements were made using matched UNICAM one centimeter cells.

pH measurements were made on a Cambridge Portable pH meter (glass electrode), which had been previously standardized at pH 4 with 0.05 M potassium acid phthalate.

Determination of Equilibrium Data. Solutions used for the study of acid base equilibria were prepared in 50 ml. volumetric flasks. Appropriate amounts of the buffer stock solutions were placed in the flasks and distilled water was added, just leaving space for the tripyridine stock solution. This was then added, the solution was diluted to the mark and then allowed to stand for at least twenty four hours to insure that the solution came to equilibrium. These solutions were then measured spectrophotometrically against standard solution which contained identical amounts of the buffer solutions. The pH of each solution was determined on the pH meter either just before or just after the spectral study.

The ferrous-tripyridine complex also was studied spectrophotometrically. Solutions were prepared in a similar manner to that discribed above. The buffers were placed in a 50 ml. flask and partially diluted, then the ferrous ion followed by the tripyridine stock solutions were added. The solution was diluted to the mark and allowed to stand for twenty four hours. These solutions were compared with standards containing the same buffers. pH measurements were made as above.

Determination of Kinetics Data. The rates of reaction for the formation and dissociation of the ferrous-tripyridine chelate were studied spectrophotometrically. For the study of the formation of the complex, solutions were prepared in the manner discribed above; as soon as the solution was prepared, it was shaken vigorously and a sample was placed in a cell. Zero time was taken when one half of the base had been added. Absorption measurements were taken at intervals on the same sample until there was no further change in absorption. The final reading was then checked using a fresh sample.

The rate of dissociation was determined by first preparing a concentrated solution of the chelate at high pH (where little dissociation occurs). Aliquots of this solution were then diluted to the usual strength for spectrophotometric measurements, at a sufficiently low pH that a considerable amount of dissociation would occur. The dissociation reaction was followed spectrophotometrically until equilibrium was established.

CALCULATIONS AND RESULTS

A.- The Acid Base Equilibria

The BH_2^{++} form shows a maximum at $\lambda = 288.5$, where ϵ_{max} is 2.180 at pH $< 1,5$, and falls off to $\epsilon_{min} = 1.440$ at $\lambda = 281.0$, pH = 4.30. A maximum of $\epsilon = 1.739$ is shown by the form BH^+ at $\lambda = 321.5$ to 323.0 with pH < 3.0; this falls off to $\epsilon_{min} = 0.603$ at $\lambda = 313$, pH > 11.0. The free tripyridine (B) shows maximum absorption, $\epsilon = 1.600$, at $\lambda = 275$, pH > 5.5. (Fig. 2)

A plot of extinction coefficient versus pH (Figs. 3 and 4) shows the transition in the forms of the base and also gives the extinction coefficient of each form.

Calculations: The pKa values were calculated from the final equations of the following derivations.

$$BH_2^{++} \rightleftharpoons BH^+ + H^+$$

$$BH^+ \rightleftharpoons B + H^+$$

where B = 2,2',2" tripyridine.

Thus:
$$k_1 = \frac{(BH^+)\ (H^+)}{(BH_2^{++})} \qquad (1)$$

$$k_2 = \frac{(B)\ (H^+)}{(BH^+)} \qquad (2)$$

Let ϵ_x equal the total Molar (tripyridine) extinction coefficient, and let α be the fraction of BH^+ dissociated. Therefore from: (2)

$$k_2 = \frac{(H^+)\ C\alpha}{C(1-\alpha)} = \frac{(H^+)\alpha}{1-\alpha} \qquad (3)$$

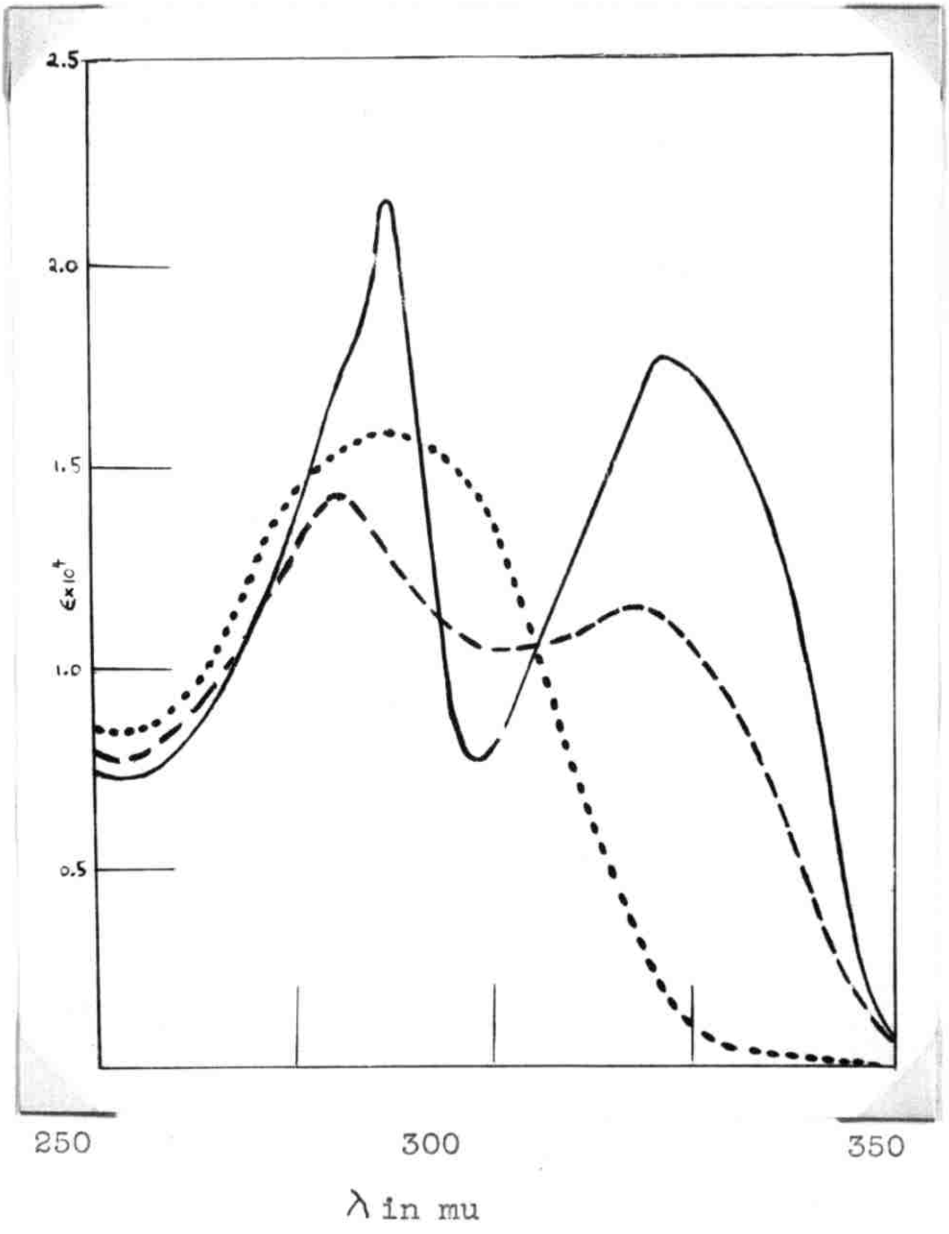


Fig.2.- Ultraviolet spectra of 2,2',2" tri-pyridine.

——— pH = 1.05
– – – pH = 4.30
····· pH 11.0

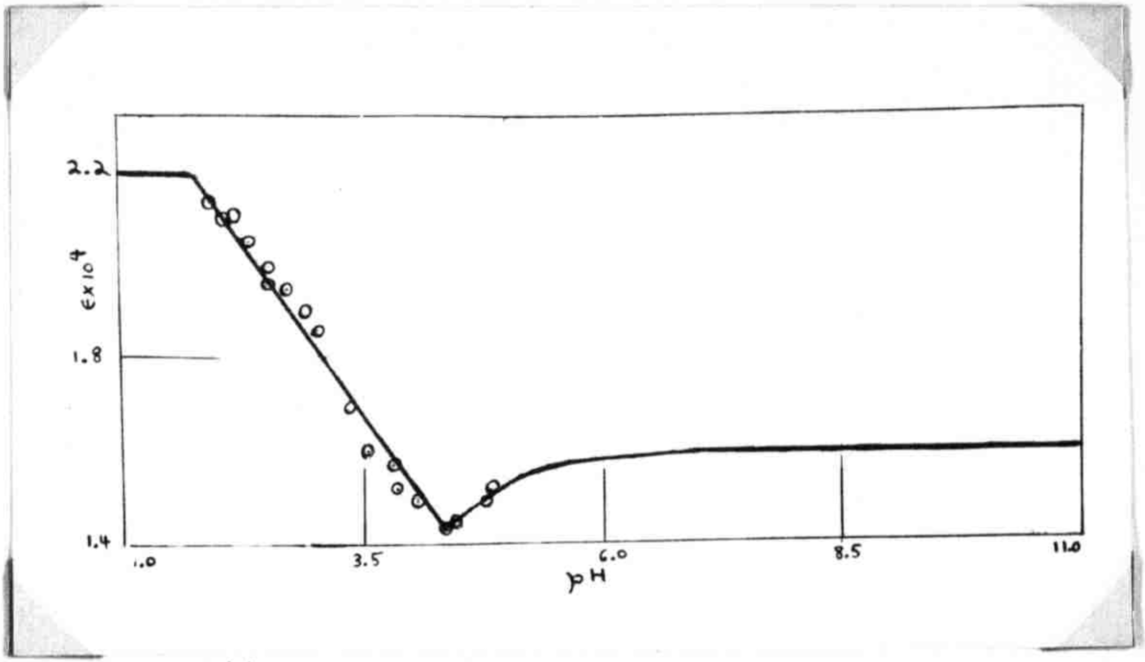


Fig.3.- BH_2^{++} Change in extinction coefficient with pH.

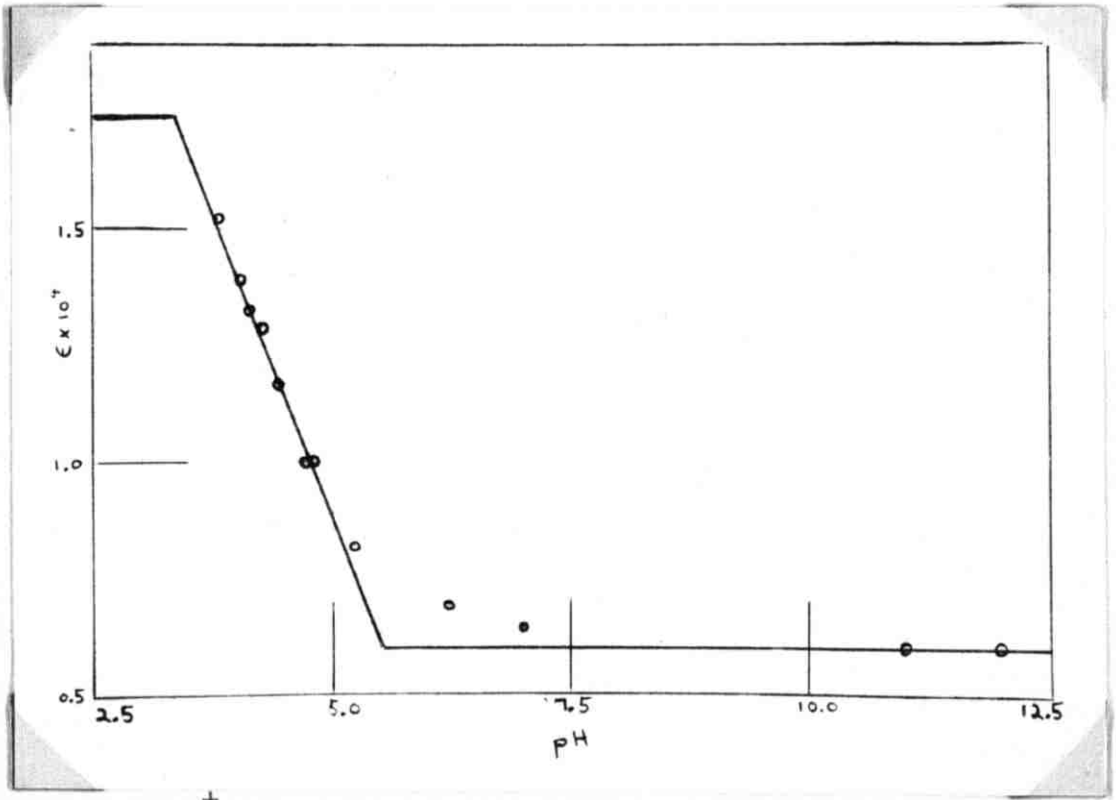


Fig.4.- BH^+ Change in extinction coefficient with pH.

$$\epsilon_x = (1 - \alpha)\, \epsilon_{BH^+} + \alpha \epsilon_B$$

$$\alpha = \frac{\epsilon_{BH^+} - \epsilon_x}{\epsilon_{BH^+} - \epsilon_B} \qquad (4)$$

Substitution of equation (4) in (3), followed by rearrangement, results in:

$$k_2 = \frac{(H^+)\ (\epsilon_{BH^+} - \epsilon_x)}{(\epsilon_x - \epsilon_B)} \qquad (5)$$

But, for the thermodynamic dissociation constant, K_2

$$K_2 = \frac{(aH^+)\ (\epsilon_{BH^+} - \epsilon_x)\ (\gamma_{\mathbf{B}})}{(\epsilon_x - \epsilon_B)\ (\gamma_{BH^+})} \qquad (6)$$

In this case, γ_B can be assumed equal to unity and γ_{BH^+} is the ionic activity coefficient of BH^+. Equation (6) can be expressed in the logarithmic form:

$$pK_2 = pH + \log \left[\frac{\epsilon_x - \epsilon_B}{\epsilon_{BH^+} - \epsilon_x}\right] + \log \gamma_{BH^+} \qquad (9)$$

where: the value of log γ_{BH^+} by the Debye Huckle limiting law is:

$$\log \gamma_{BH^+} = -\ (0.509)\ (1)\ (I^{\frac{1}{2}})/(1 + I^{\frac{1}{2}})$$

where I is the ionic strength of the solution.

In a similar manner, the expression for pK_1 can be derived from equation (1). The final equation is:

$$pK_1 = pH + \log \left[\frac{\epsilon_x - \epsilon_{BH^+})}{\epsilon_{BH_2^{++}} - \epsilon_x}\right] + \log \left[\frac{\gamma BH_2^{++}}{\gamma BH^+}\right]$$

$$\log \gamma_{\text{Total}} = -(0.509)(3)\, I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$$

Table III

Data and Calculations for the Determination of pK_1 ($pK_{BH_2^{++}}$)

pH	λ	$\epsilon_x \times 10^4$	I	$\log \gamma$	$\log \left[\frac{\epsilon_x - \epsilon_{BH^+}}{\epsilon_{BH_2^{++}} - \epsilon_x} \right]$	pK_1
1.92	288.5	2.128	0.11	-0.381	1.122	2.66
2.02	288.0	2.098	0.11	-0.381	0.904	2.54
2.15	288.0	2.100	0.10	-0.368	0.916	2.70
2.30	288.0	2.042	0.10	-0.368	0.640	2.57
2.49	288.0	1.991	0.10	-0.368	0.464	2.59
2.50	288.0	1.958	0.10	-0.368	0.369	2.50
2.69	288.0	1.944	0.10	-0.368	0.329	2.65
2.87	288.0	1.898	0.10	-0.368	0.210	2.71
3.00	288.0	1.858	0.10	-0.368	0.112	2.74
3.36	288.0	1.692	0.10	-0.368	-0.286	2.71
3.52	287.5	1.601	0.10	-0.368	-0.556	2.60
3.81	280.0	1.570	0.10	-0.368	-0.661	2.78
3.86	281.0	1.520	0.10	-0.368	-0.916	2.58
4.05	281.0	1.493	0.10	-0.368	-1.112	2.57

For the form BH_2^{++}

$\epsilon_{max} = 2.180 \times 10^4$ $\lambda = 288.5$ mμ pH < 1.5

$\epsilon_{min} = 1.440 \times 10^4$ $\lambda = 281.0$ mμ pH $= 4.30$

Thus for the equilibrium $BH_2^{++} \rightleftharpoons BH^+ + H^+$, the pK_1 value is 2.64 ± 0.07.

Table IV

Data and Calculations for the Determination of PK_2 (pK_{BH^+})

pH	λ	$\epsilon_x x 10^4$	I	$\log \gamma$	$\log \left[\frac{\epsilon_x - \epsilon_B}{\epsilon_{BH^+} - \epsilon_x} \right]$	pK_2
3.81	321.5	1.526	0.10	-0.123	0.638	4.33
4.05	320.0	1.392	0.10	-0.123	0.356	4.28
4.15	319.0	1.326	0.10	-0.123	0.243	4.27
4.30	319.0	1.288	0.10	-0.123	0.182	4.36
4.43	318.5	1.161	0.10	-0.123	-0.008	4.30
4.72	314.0	0.995	0.10	-0.123	-0.278	4.32
4.78	314.0	0.995	0.10	-0.123	-0.278	4.38
5.16	314.0	0.811	0.10	-0.123	-0.659	4.38

For the form BH^+:

$\epsilon_{max} = 1.739 \times 10^4$ $\lambda = 321.5$ to 323.0 mμ $pH < 3.0$

$\epsilon_{min} = 0.603 \times 10^4$ $\lambda = 313.0$ mμ $pH > 11.0$

Thus for the equilibrium $BH^+ \rightleftharpoons B + H^+$, the pK_2 value is 4.33 ± 0.03.

The sum of the values for pK_1 and pK_2 gives the composite $pK_{1,2}$ equal to 7.0 ± 0.1

B.- The Ferrous-Tripyridine Complex

The iron (II) tripyridine complex 5 and 6 exhibits three measurable maxima. (Fig.5,6) In the ultra violet region, these come at $\lambda = 273$ and $\lambda = 318$. In both cases there is interference due to absorption in these regions by the free base and by its protonic forms. Another peak was observed below $\lambda = 230$, but the limitations of the instrument prevented any conclusions being drawn. In the visible region, one maximum occurs, at $\lambda = 556$. Here there is no interference, as the free tripyridine does not absorb in the visible region.

The absorption data at λ 556 was used for the determination of pK_D for the complex. The complex was found to obey Beer's Law (Fig. 7) and by use of solutions containing excess of one component (i.e. base or Fe^{++}) the molar extinction coefficient (ϵ) of the complex was calculated as 11630.

The pK_D values for the complex Ferrous di-2,2',2" tripyridine were calculated from the final expressions of the following derivation.

Assume: $$FeB_2^{++} \rightleftharpoons Fe^{++} + 2B \tag{10}$$

$$K'_D = \frac{(Fe^{++})\ (B)^2}{(FeB_2^{++})} \tag{11}$$

$C_{Fe^{++}}$ and C_B are the analytical concentrations of Fe^{++} and B; (Fe^{++}), (B), (FeB_2^{++}) are the concentrations in the form shown; then:

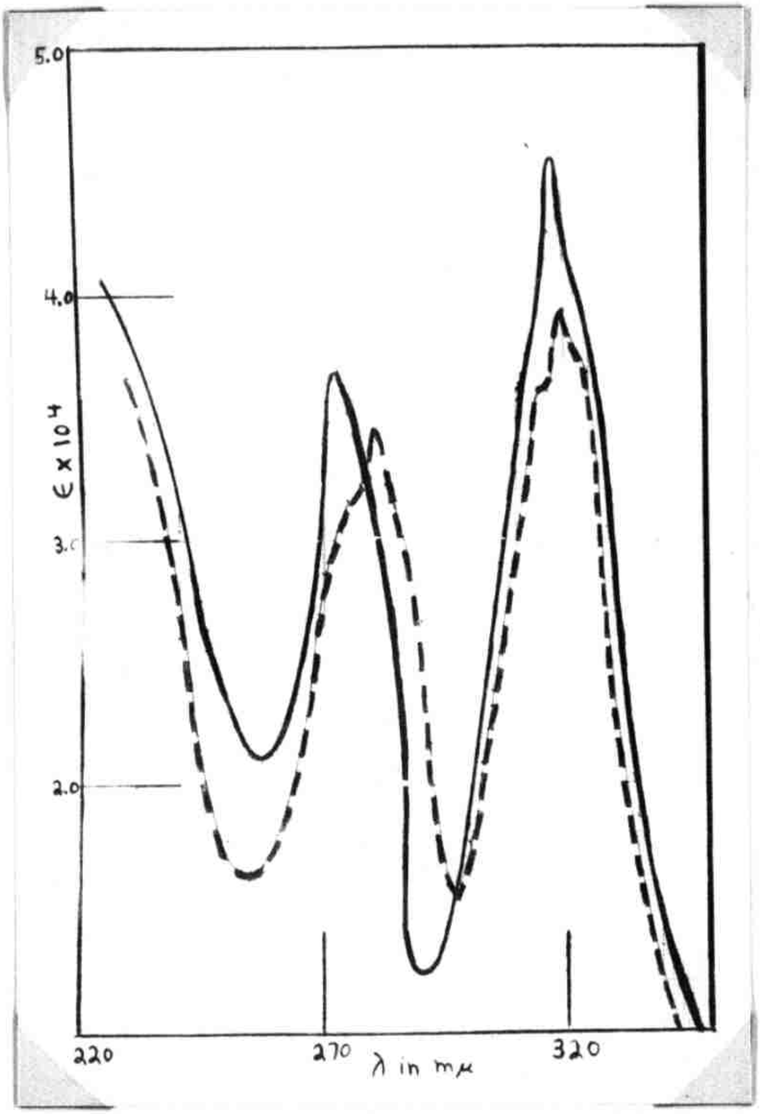


Fig.5.- Ultraviolet spectra of $FeB_2H_2{}^{4+}$

——— pH = 6.32
– – – pH = 1.04

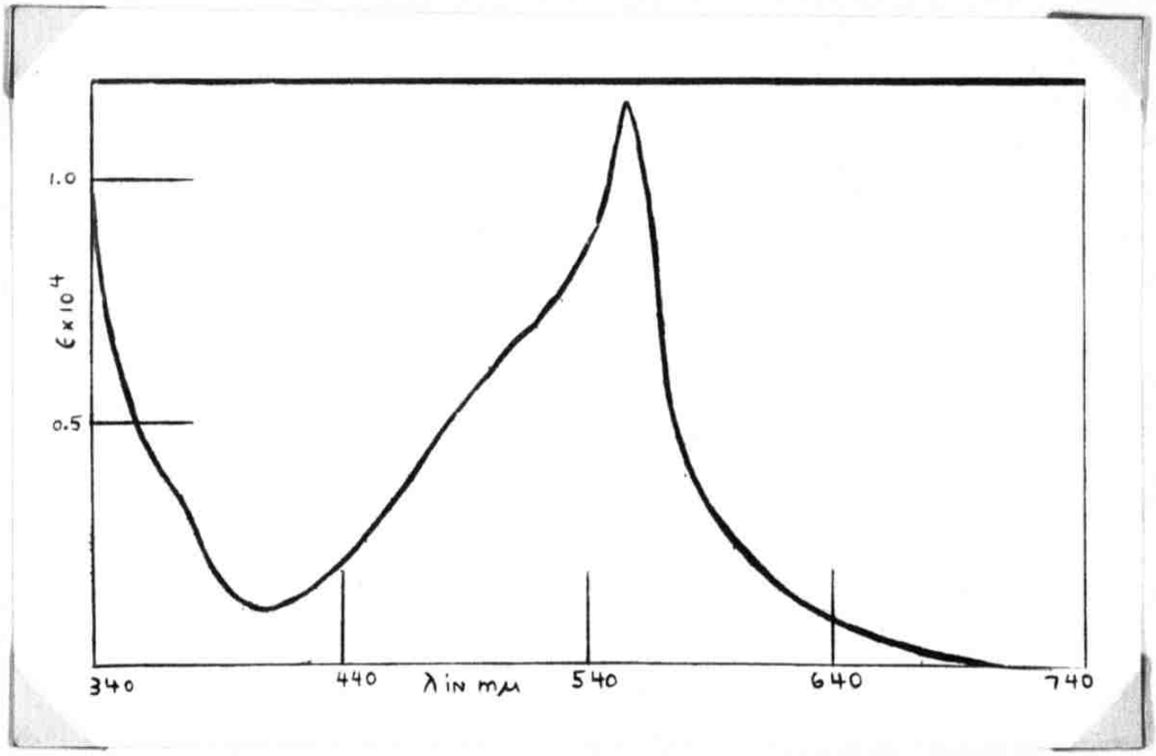


Fig.6.- Visible spectra of $FeB_2H_2^{4+}$, pH = 5.61.

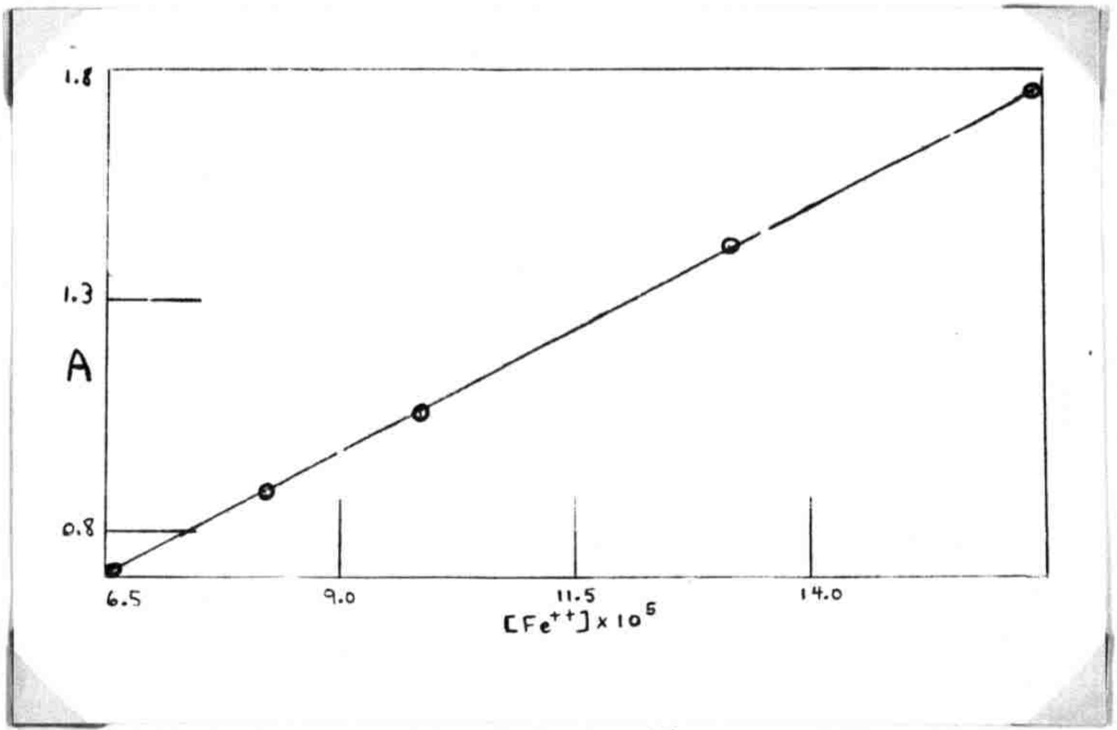


Fig. 7.- Beer's Law plot of $FeB_2H_2^{4+}$

$$(Fe^{++}) = C_{Fe^{++}} - (FeB_2^{++})$$

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

$$K_2 = (B)(H^+)/(BH^+) \qquad K_{1,2} = (B)(H^+)^2/(BH_2^{++})$$

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

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

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

Since $(FeB_2^{++}) = \dfrac{A}{\epsilon_{FeB_2^{++}}}$, (B) and (Fe^{++}) can be substituted in equation (11) and K_D' calculated.

$$pK_D' = -\log K_D'$$

pK_D' was found to vary inversely as pH (Fig. 8). The plot was extrapolated to zero pH, indicating that pK_D' should be about 20.6. It then appeared tha pK_D was equal to the sum of pK_D' and twice the pH.

Thus:

$$FeB_2H_2^{4+} \rightleftharpoons Fe^{++} + 2B + 2H^+$$

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

Therefore,

$$pK_D = pK_D' + 2pH$$

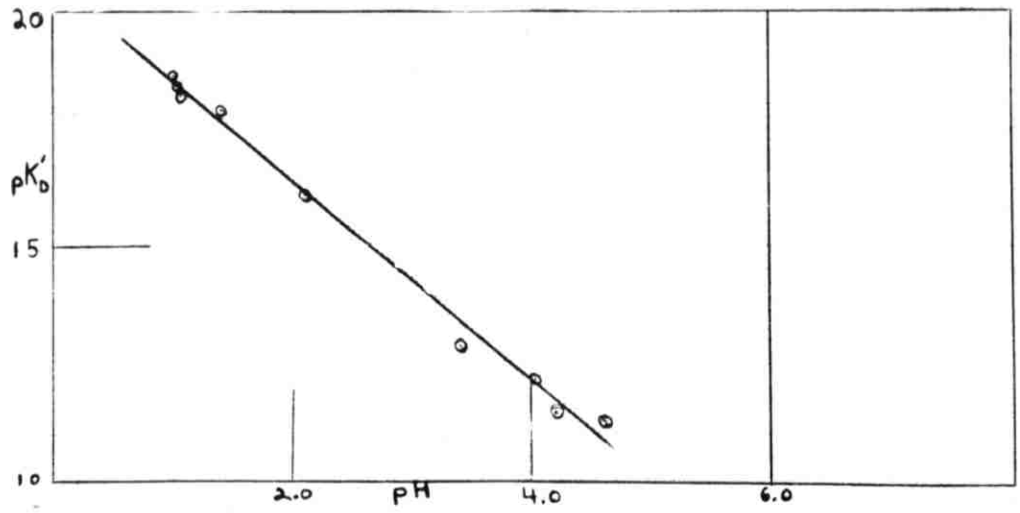


Fig.8.- Plot of calculated pK_D' of ferrous tripyridine complex vs pH of the solution.

Table V

Data and Results for the Determination of pK_D

pH	A	A/ϵ $M \times 10^{-4}$	$C_{Fe^{++}}$ $M \times 10^{-4}$	C_B $M \times 10^{-4}$	(Fe^{++}) $M \times 10^{-4}$	(B)	pK_D'	pK_D
0.98	0.882	0.755	1.221	2.442	0.366	6.98×10^{-10}	18.63	20.59
1.02	0.980	0.842	1.221	2.442	0.379	8.80×10^{-10}	18.46	20.50
1.05	0.954	0.819	1.221	2.442	0.402	1.06×10^{-9}	18.26	20.36
1.38	1.143	1.010	1.221	2.442	0.211	2.47×10^{-9}	17.90	20.66
2.10	1.228	1.070	1.221	2.442	0.151	2.53×10^{-8}	16.04	20.24
3.43	1.333	1.146	1.221	2.442	0.075	1.55×10^{-6}	12.81	19.67*
4.02	1.352	1.162	1.221	2.442	0.059	3.72×10^{-6}	12.15	20.19
4.20	1.335	1.148	1.221	2.442	0.076	6.21×10^{-6}	11.40	20.00
4.61	0.883	0.760	0.820	1.641	0.060	7.83×10^{-6}	11.31	20.53

Average $pK_D = 20.4 \pm 0.2$

* not included in average value

C.- Kinetics

The reaction rates for the formation and dissociation of the ferrous tripyridine complex were followed spectrophotometrically.

$$Fe^{++} + 2B + 2H^{+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} FeB_2H_2{}^{4+}$$

The rate of formation was easily followed in solutions buffered at low pH and containing at least five parts of tripyridine to one part of ferrous ion. Under these conditions the reaction went to completion; thus the possibility of a complicated reverse reaction was eliminated. It was necessary, that the pH be lower than 1.5, otherwise the reaction would reach equilibrium too quickly to be followed.

Since the solutions were buffered, the hydrogen ion concentration could be considered to be constant with respect to the amount of hydrogen ion taking part in the reaction. The base was in excess analytically but existed in the form $BH_2{}^{++}$ with about 0.01% in the form of the free base. There was no evidence that the concentration of the free base changed during the time required for the reaction to come to equilibrium. Therefore, if the reaction rate is dependent upon the concentration of ferrous ion only, the rate of the reaction can be determined:

$$-d(\mathrm{Fe}^{++})/dt = k_f(\mathrm{Fe}^{++})(B)^2(H^+)^2$$

But if (B) and (H^+) are constant,

$$-d(\mathrm{Fe}^{++})/dt = k_f'(\mathrm{Fe}^{++})$$

Rearranging and integrating gives:

$$2.303 \log (\mathrm{Fe}^{++}) = k_f' t + \text{constant}$$

But $(\mathrm{Fe}^{++}) = C_{\mathrm{Fe}^{++}} - C_c$ where $C_{\mathrm{Fe}^{++}}$ is the analytical concentration of ferrous ion and C_c is the concentration of the complex at time t. C_c is a function of the absorption at time t, therefore:

$$C_c = A_t/\epsilon$$

If the log of $(C_{\mathrm{Fe}^{++}} - C_c)$ is plotted against time, a straight line is obtained if the reaction is first order. The slope of this line times 2.303 is equal to k_f'. Then:

$$k_f = k_f'/(B)^2(H^+)^2$$

Based on this analysis, k_f was determined at pH = 1.17. The slope of the plot (Fig. 9) is 0.11 min.^{-1}, thus:

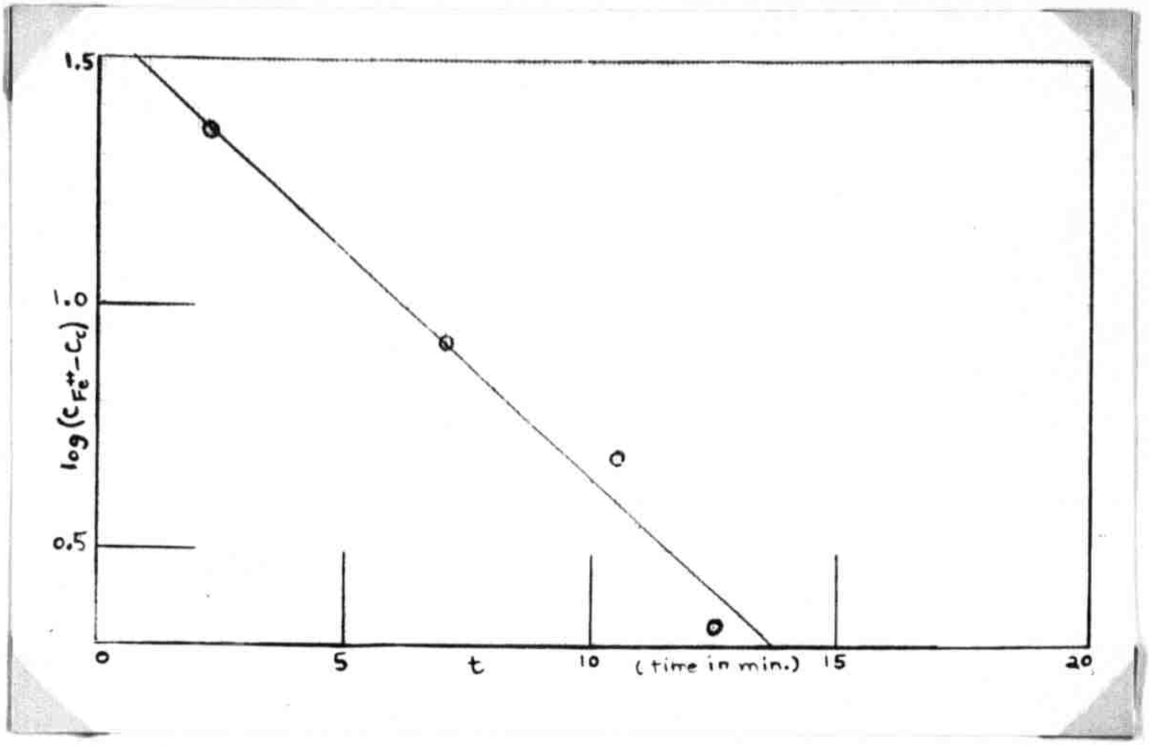
$$k_f' = 2.303 \times 0.11 = 0.253 \text{ min.}^{-1}$$

At pH = 1.17, (B), calculated from the equilibrium constant and the analytical concentration of the base, was equal to 1.43×10^{-8}. Therefore:

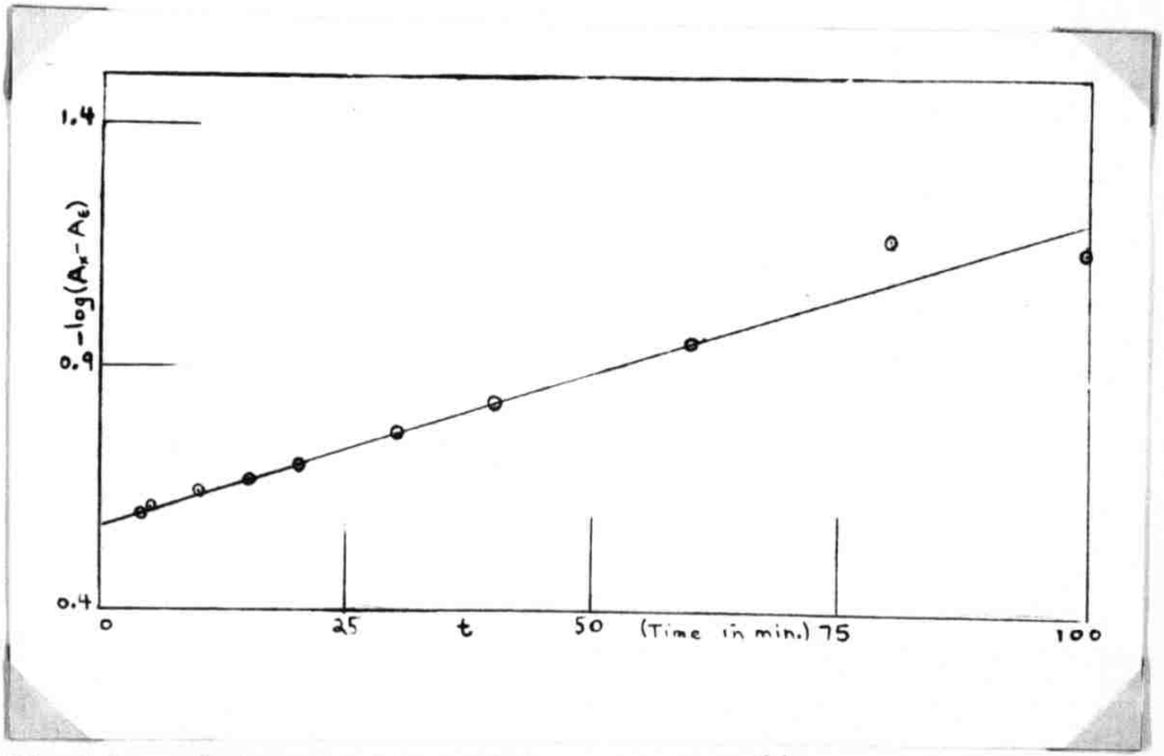
$$k_f = 0.253 \text{ min.}^{-1} / (1.43 \times 10^{-8})^2(6.75 \times 10^{-2})^2$$

$$k_f = 2.7 \times 10^{17} \ (M/l)^{-4} \text{ min.}^{-1}$$

The decomposition of the complex was followed in the manner described in the experimental section. In determining the rate of dissociation, the problem was complicated by a strong opposing reaction.



<u>Fig.9</u>.- Determination of k_f of $FeB_2H_2^{4+}$.



<u>Fig.10</u>.- Determination of k_d of $FeB_2H_2^{4+}$.

$$FeB_2H_2^{4+} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Fe^{++} + 2B + 2H^+$$

Assuming that the tripyridine and hydrogen ion concentrations were constant throughout the reaction,

$$-dC/dt = k_d(C) - k_f(Fe^{++})$$

$$-dC/dt = k_d(C_c) - k_f(C_{Fe^{++}} - C_c) \qquad (12)$$

Where C_c is the concentration of the complex at time t; $C_{Fe^{++}}$ is the analytical concentration of ferrous ion.

At equilibrium, $-dC/dt = 0$, therefore:

$$k_d(C_e) = k_f(C_{Fe^{++}} - C_e)$$

$$k_f = k_d(C_e)/(C_{Fe^{++}} - C_e) \qquad (13)$$

Where C_e is the concentration of the complex at equilibrium.

Substitution of (13) in (12) gives:

$$-dC/dt = k_dC - \frac{k_dC_eC_{Fe^{++}} - k_dC_eC_c}{C_{Fe^{++}} - C_e}$$

With rearrangement this becomes:

$$-dC/dt = \frac{k_d(C_{Fe^{++}})(C_c - C_e)}{C_{Fe^{++}} - C_e}$$

With integration:

$$\ln(C_c - C_e) = \frac{k_d(C_{Fe^{++}})\ t}{C_{Fe^{++}} - C_e} + \text{constant} \qquad (14)$$

Thus: $2.303 \times \text{slope} = k_d(C_{Fe^{++}})/(C_{Fe^{++}} - C_e)$

$$k_d = 2.303(\text{slope})(C_{Fe^{++}} - C_e)/(C_{Fe^{++}}) \qquad (15)$$

From this derivation the rate of dissociation of the complex was determined. Equation (14) requires a plot of log $(C_c - C_e)$ versus time. However;

$$C_c = A_c/\epsilon \quad \text{and} \quad C_e = A_e / \epsilon$$

Therefore log $(A_c - A_e)$ could be plotted against time.

At pH = 1.27 and $C_{Fe^{++}} = 1.221 \times 10^{-4}$, the slope was equal to 6.3×10^{-3}. Substitution in equation (15) gives:

$$k_d = \frac{2.303(6.3 \times 10^{-3})(1.221 \times 10^{-4} - 1.03 \times 10^{-4})}{1.221 \times 10^{-4}}$$

$$k_d = 2.26 \times 10^{-3} \text{ min.}^{-1}$$

From these rate constants, K_D for the equilibrium can be calculated.

$$K_D = k_d/k_f = (2.26 \times 10^{-3})/(2.7 \times 10^{17})$$

$$K_D = 8.4 \times 10^{-21} \quad \ldots\ldots \quad pK_D = 20.1$$

This value compares favourably with the value $pK_D = 20.4$ which was calculated from the purely equilibrium study.

DISCUSSION

In their study of 2,2',2" tripyridine Brandt and Wright (5) determined the composite pK_a value as 7.1 for the addition of two protons to each molecule of the base. The work was done by potentiometric and conductometric methods, but neither gave any inflection to indicate the addition of only one proton. The study here under discussion made use of spectrophotometric methods and it was possible to study the equilibrium for the addition of each proton.

For the removal of one proton from the diprotonic form of tripyridine pK_1 equals $2.64 + 0.07$ and removal of the second proton has a pK_2 value of 4.33 ± 0.03. In these determinations the difference in precision of the two values may be explained by the fact that the distance between, ϵ_{max} and ϵ_{min} is much less for the form BH_2^{++} than for BH^+ (Fig. 3 & 4) and also that the pH values are more critical in determination of K_1.

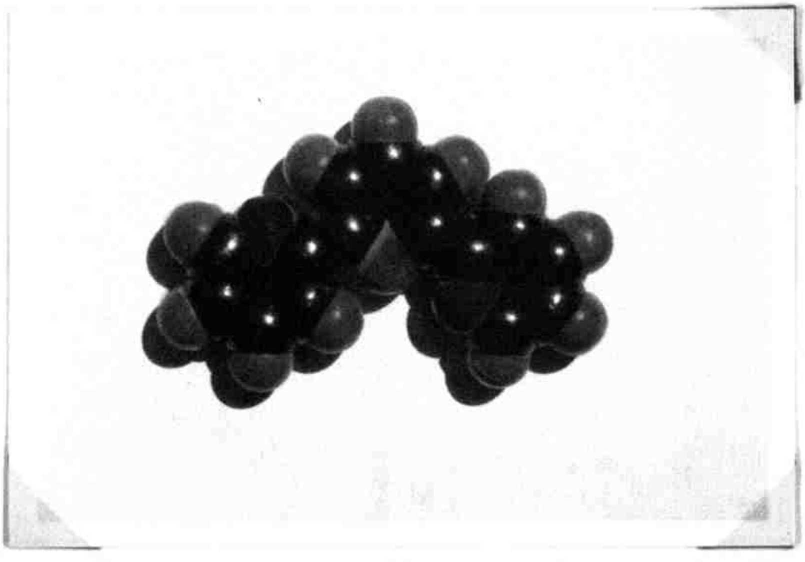
The composite pK_a of 7.0 ± 0.1 here determined compares favorably with Brandt's value of 7.1 (4). There is no indication in Brandt's report whether allowance was made in the calculation for ionic strength of the solution. If the value is yet to be adjusted to zero ionic strength, then his reported value is somewhat high.

This study yielded no conclusive evidence of the addition of a third proton to each molecule of tripyridine. A maximum was observed in all spectra in the range λ = 230 to 235 with ϵ near 18000. This might indicate the formation of tripyH_3^{+++}; however, no conclusions can be drawn as the spectra below λ = 240 are too uncertain.

It is quite possible that a third hydrogen is not added. If we assume resonance across the internuclei bonds, giving partial π bond character; we can postulate that the molecule is practically planar. Thus there is the possibility of three geometric isomers (Fig. 11). In all three cases, the addition of a third proton is unlikely. In case A one proton is added easily and the second with some difficulty; but the third proton should have great difficulty in attaching itself, being repelled by the charge and also being sterically hindered by the first two protons. In cases B and C there should be little difficulty in forming the diprotonic form, but electrical repulsion in case B and steric hindrance in both cases probably prevents addition of a third hydrogen ion.

The study of the ferrous 2,2',2" tripyridine system indicated that between pH of 0.98 and 4.61, the chelate formed is $FeB_2H_2{}^{4+}$. It is interesting to note that several workers have postulated the existence in acid solutions of one proton in the ferrous 2,2'bipyridine

Case A



Case B

Fig.11.- Fisher-Taylor-Hirschfelder models of three geometric isomers of 2,2',2" tripyridine.

Case C

complex (2,8,9).

In buffered solutions outside the 0.98 to 4.61 pH range, reproducible results were not obtained, possibly indicating a transition in the nature of the complex. Use of NaOH solutions of pH 10 to 12 resulted in the formation of ferric hydroxide. The pH range above the limit of acetate buffers was not studied because the only available, non absorbing buffer reagent, phosphate, interfers with the complex formation of tripyridine (15).

The study of the kinetics of the complex formation and dissociation should aid in elucidation of the mechanism. The dissociation appeared to envolve the breaking down of the complex $FeB_2H_2^{4+}$ with the opposing reaction being quite significant. With this latter factor taken into consideration, the dissociation rate constant was found to be first order, $k_d = 2.26 \times 10^{-3}$ min.$^{-1}$.

Although the formation of the complex, especially in the presence of excess base, is very rapid, it was possible to follow the reaction in acid solutions. The formation was found to be first order with respect to ferrous ion; the concentration of the hydrogen ions and the base appeared to be constant. $k_f = 2.7 \times 10^{17}$.

After calculating the two rate constants, the equilibrium constant was determined as $K_D = 8.4 \times 10^{-21}$ or $pK_D = 20.1$. This value compares favorably with the value of 20.4 obtained from the equilibrium studies.

Since these two independently determined equilibrium constants are in fair agreement, some indication is given of the mechanism of the reaction. The formation of the complex was very slow in acid solution but became fairly constant above pH 3.5. Therefore it is unlikely that the formation of the complex progresses thru either the BH_2^{++} form or the BH^+, although the latter is possible. However, were the reaction between ferrous ion and two molecules of BH^+:

$$Fe^{++} + 2BH^+ \rightleftharpoons FeB_2H_2^{4+}$$

then the formation constant would be of the order of magnitude of 10^{11} to 10^{12}. Were this the case, calculation of K_D from rate constants would give a **value** of roughly 10^{-15}. This contradicts the equilibrium K_D value and may be eliminated.

Thus there is left a third possiblity, formation of the complex from the simple ions.

$$Fe^{++} + 2B + 2H^+ \rightleftharpoons FeB_2H_2^{4+}$$

In view of the agreement of K_D values calculated from this assumption, and considering the greater speed at which the reaction reaches equilibrium in basic solution, this appears to represent the mechanism.

Use of excess tripyridine in solution with ferrous ion resulted in the reaction effectively going to completion if the ratio of base to iron is at least 5:1. The molar extinction coefficient of the complex is 11600 at $\lambda = 556$.

This allows for detection of ferrous ion present in solution in concentration, as low as two parts per million. However, there is one restriction, that the pH range be 3.5 to 4.5 because in this range the reaction appears to go to completion in the presence of excess tripyridine. Thus for use in the visible region, tripyridine is comparable to 1,10 phenanthroline which absorbs at $\lambda = 510$, $\epsilon = 11,100$ (15) and slightly superior to 2,2' bipyridine for which $\epsilon = 8650$ at $\lambda = 522$.

The ultra violet region also offers possible use in analytical work. Calculations from spectra (Figs.2,5,6) give the extinction coefficient of the ferrous complex as 47000 at $\lambda = 318$. In this region the protonic forms of the tripyridine (BH_2^{++},BH^+) absorb strongly with an average extinction coefficient of 16000. The free base also absorbs in this region, though not as strongly.

Another maximum is shown by the complex at $\lambda = 273$. Calculation from the spectra gave the extinction coefficient of the complex as 37000. In this region BH_2^{++} and free base both absorb with an average extinction coefficient of 13000. Therefore in both the above cases, use as an analytical method for determination of iron would be very difficult as the presence of any excess base would make calculations quite complicated.

A general disadvantage involved in the use of tripyridine as an analytical reagent is the fact that it is expensive and is not available commercially in the pure state. The latter factor requires that the reagent be purified before use but no efficient method of purification is known. This disadvantage, combined with the limited pH range through which tripyridine can be used as an analytical reagent, overshadows any advantage gained by the fact that the extinction coefficient of tripyridine is slightly higher than those of 1,10 phenanthroline and 2,2' bipyridine.

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