we have preliminary evidence[35] that the nitrate ion may be having a catalytic influence. Rate plots for this system in 1.0 $F$ $HClO_4$ or 0.5 $F$ $H_2SO_4$ also exhibit negative deviation from linearity, but the values of the rate constants calculated from the initial slopes are about 60% lower.

A possible reaction scheme consistent with the above observations is outlined in Figure 5. Paths A–E all contribute to the formation of halide ion and our qualitative observations suggest that A, B, and E predominate. It is not possible from the present data to analyze this scheme more completely but the mode of hydrolysis and/or isomerization of *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$ is under investigation.

**Acknowledgment.**—We acknowledge with thanks funds from the New Zealand Universities Grants Committee for the purchase of instruments used in this research. M. C. C. thanks British Petroleum (N. Z.) Ltd. for the receipt of a scholarship.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SYRACUSE UNIVERSITY, SYRACUSE, NEW YORK 13210

# The Formation Constant of Bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine]iron(II). Evidence for Formation of a Protonated Bis Complex

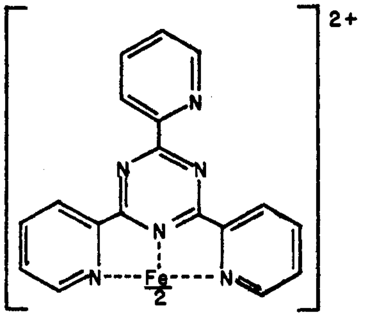
BY FREDERICK H. FRASER,* PAUL EPSTEIN,[1] AND DANIEL J. MACERO

*Received November 18, 1971*

A value of $(2.8 \pm 1.2) \times 10^{11}$ for the formation constant of bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine]iron(II), $Fe(TPTZ)_2^{2+}$, was determined from the pH dependence of the conditional formation constant which was spectrophotometrically evaluated. Spectroscopic evidence for the formation of a protonated bis complex, $Fe(TPTZ)_2H^{3+}$, was observed at high hydrogen ion concentrations (pH 1.3–2.0) and at a ligand-to-metal mole ratio of 25. Inclusion of the formation of $Fe(TPTZ)_2H^{3+}$ was necessary to rationalize the pH dependence of the conditional formation constant of $Fe(TPTZ)_2^{2+}$. A value of $(2.5 \pm 1.1) \times 10^2$ for the formation constant of $Fe(TPTZ)_2H^{3+}$ was determined.

## Introduction

The tridentate ligand 2,4,6-tri(2-pyridyl)-1,3,5-triazine, TPTZ, which resembles terpyridine, was first synthesized by Case and Koft.[2] Diehl, *et al.*,[3] first characterized the bis complex of this ligand with iron(II). The high molar absorptivity in aqueous solution at 593 nm has led to the utilization of the complex formation in iron(II) determinations.[3–6] Kratochvil and White[7] made use of the rapid reaction between EDTA and $Fe(TPTZ)_2^{2+}$ in determining trace amounts of EDTA, and Pagenkopf and Margerum[8] utilized the same reaction to characterize the formation and dissociation kinetics of $Fe(TPTZ)_2^{2+}$. The formation equilibrium was first studied by Buchanan, *et al.*[9] Evidence for any appreciable formation of the mono complex, $Fe(TPTZ)^{2+}$, has not been observed.[3,8,9]



$Fe(TPTZ)_2^{2+}$

Buchanan, *et al.*,[9] assuming TPTZ to be weakly monobasic ($K_H = 1.3 \times 10^3\ M^{-1}$), determined the formation constant of $Fe(TPTZ)_2^{2+}$ over the pH range of 1.9–2.2 to be $1.75 \times 10^{10}$. Pagenkopf and Margerum[8] assumed TPTZ to be weakly dibasic ($K_H = 3.4 \times 10^3$, $K_{2H} = 5.4 \times 10^2\ M^{-1}$) and reevaluated the formation constant, $\beta_2 = (3.0 \pm 1.8) \times 10^{12}$, over a pH range of 2.9–4.5. Prasad and Peterson[10] in the course of a study of the stability of $Co(TPTZ)_2^{2+}$ also reevaluated the basicity of TPTZ and concluded that $K_H = (8 \pm 5) \times 10^2$ and $K_{2H} = (6.58 \pm 0.01) \times 10^2$. Pagenkopf and Margerum[8] discounted the formation of a protonated bis complex on the basis of measured dissociation rates at high hydrogen ion concentrations (pH <2.0). The present study was undertaken to accurately determine the formation constant for $Fe(TPTZ)_2^{2+}$. The evidence for the formation of $Fe(TPTZ)_2H^{3+}$ was somewhat unexpected; its existence would indicate, however, that the mechanism for the acid dissociation of $Fe(TPTZ)_2^{2+}$ is more involved than that originally put forth by Pagenkopf and Margerum.[8]

## Experimental Section

Solutions of the ligand TPTZ (G. Frederick Smith Chemical Co.) were prepared by dissolving in a few drops of concentrated sulfuric acid accurately weighed quantities of the trihydrate (mol wt 366.3), which had been purified twice by recrystallization

---

[1] P. E. was a participant in the Precollege Student Science Training Program, NSF Grant No. GW-6638, held at Syracuse University during the summer of 1971.

[2] F. H. Case and E. Koft, *J. Amer. Chem. Soc.*, **81**, 905 (1959).

[3] P. F. Collins, H. Diehl, and G. W. Smith, *Anal. Chem.*, **31**, 1862 (1959).

[4] P. F. Collins and H. Diehl, *Anal. Chim. Acta*, **22**, 125 (1960).

[5] B. Zak, G. A. Cavanaugh, and L. A. Williams, *Chemist-Analyst*, **50**, 8 (1961).

[6] D. S. Fischer and D. C. Price, *Clin. Chem.*, **10**, 21 (1964).

[7] B. Kratochvil and M. C. White, *Anal. Chem.*, **37**, 111 (1965).

[8] G. K. Pagenkopf and D. W. Margerum, *Inorg. Chem.*, **7**, 2514 (1968).

[9] E. B. Buchanan, Jr., D. Crichton, and J. R. Bacon, *Talanta*, **13**, 903 (1966).

[10] J. Prasad and N. C. Peterson, *Inorg. Chem.*, **10**, 88 (1971).

(mp 248–249.5°) from a 50% ethanol–water solution. The concentrates were diluted with conductivity water ($R_s$ >1 $M$) to give 1.49 × $10^{-4}$ and 1.50 × $10^{-3}$ $M$ solutions (pH 3.4). A 1.49 × $10^{-4}$ $M$ iron(II) solution was prepared from fresh reagent grade ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ (Baker and Adamson Quality), and its pH adjusted to approximately 3.4 with concentrated sulfuric acid.

A Corning Model No. 476050 semimicro combination electrode and a Beckman Zeromatic expanded-scale pH meter were used to make the pH measurements. The system was periodically calibrated against six Coleman certified buffers ranging from a pH of 2.01 ± 0.01 to 7.03 ± 0.01. Hydrogen ion concentrations were calculated from the measured pH values assuming the activity coefficient of $H^+$ to be unity. The absorbance at 593 nm and the solution spectra of the $Fe(TPTZ)_2^{2+}$ solutions were measured in 10-mm matched Spectrosil cells with a Beckman Model DB spectrophotometer. Continuous solution spectra were recorded on a Moseley Autograf Model 7001A X-Y recorder. Calculation of $\beta_2$ for $Fe(TPTZ)_2^{2+}$ from the experimental results was carried out on an IBM-360-50 computer using an APL 360 program.

Solutions for a continuous-variations analysis of $Fe(TPTZ)_2^{2+}$ at pH 3.7 ± 0.3 were prepared by mixing 0.250–4.750 ml of the stock 1.49 × $10^{-4}$ $M$ TPTZ solution with 4.750–0.250 ml of the 1.49 × $10^{-4}$ $M$ iron(II) solution. The varying volumes were delivered from separate 5.000 ± 0.006 ml burets into 10.00 ± 0.02 ml volumetric flasks which were then brought to volume with conductivity water. Thus, the concentration constant, $k = C_{Fe} + C_{TPTZ}$, where $C_{Fe}$ and $C_{TPTZ}$ are the analytical concentrations of iron(II) and TPTZ, respectively, was maintained at 7.49 × $10^{-5}$ $M$ throughout the entire series of continuous-variations measurements. The absorbance at 593 nm of each solution in this series was normalized by the method proposed by Momoki, *et al.*:[11] $y = A_{exp}/A_{max}$, where $y$ is the normalized absorbance, $A_{exp}$ is the absorbance of the sample solutions, and $A_{max}$ the absorbance of a solution with $C_{Fe}$ identical with that of a sample solution with a ligand mole fraction of 0.66 but with $C_{TPTZ}$ much greater ($\sim 10k$).

Solutions for the measurement of the pH dependence of the conditional formation constant, $\beta'$, were prepared by mixing together 1.000 ± 0.006 ml of the 1.49 × $10^{-4}$ $M$ iron(II) solution and 2.000 ± 0.006 ml of the 1.49 × $10^{-4}$ $M$ TPTZ solution in 10.00 ± 0.02 ml volumetric flasks. The pH of each solution was adjusted by adding small volumes of sulfuric acid or sodium hydroxide before bringing the flasks to volume with conductivity water. The ionic strength of the solutions varied from 0.028 to 0.00016. No attempt was made to maintain a constant ionic strength, since Diehl, *et al.*,[3] had observed that the formation of $Fe(TPTZ)_2^{2+}$ has a high tolerance for sodium, potassium, and sulfate ions, and since we also observed[12] that equilibria associated with the formation of $Fe(TPTZ)_2^{2+}$ such as $Fe(TPTZ)_2^{2+} + Hg^{2+} \rightleftarrows Hg(TPTZ)_2^{2+} + Fe^{2+}$ are unaffected by large concentrations of $Na_2SO_4$.

The measured absorbances were normalized against the absorbance of a solution (pH 4.0) prepared by mixing together 1.000 ± 0.006 ml of the 1.49 × $10^{-4}$ $M$ iron(II) solution and 5.00 ± 0.01 ml of the 1.50 × $10^{-3}$ $M$ TPTZ solution. The conditional formation constant, $\beta'$, was calculated using the normalized absorbance method described by Likussar and Boltz,[13] which has the advantage that a knowledge of the molar absorptivity is not required. The thermodynamic formation constant, $\beta_2$, was calculated from the pH dependence of $\beta'$ by the method described by Ringbom[14] and Butler.[15]

Continuous solution spectra of solutions prepared by mixing 1.000 ± 0.006 ml of the 1.49 ± $10^{-4}$ $M$ iron(II) solution and 5.00 ± 0.01 ml of the 1.50 × $10^{-3}$ $M$ TPTZ solution were examined over a pH range of 1.3–2.2. The wavelength of the main absorption peak and its shoulder were examined as a function of pH. All measurements were made at room temperature (20 ± 2°).

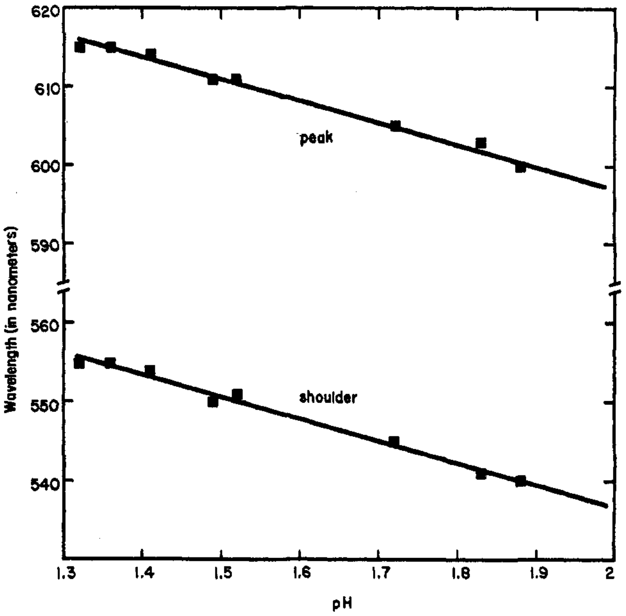


Figure 1.—The observed shift of the wavelengths of the main and shoulder peaks with pH. $[Fe^{2+}] = 1.49 \times 10^{-5}$ $M$ and $[TPTZ] = 7.45 \times 10^{-4}$ $M$.

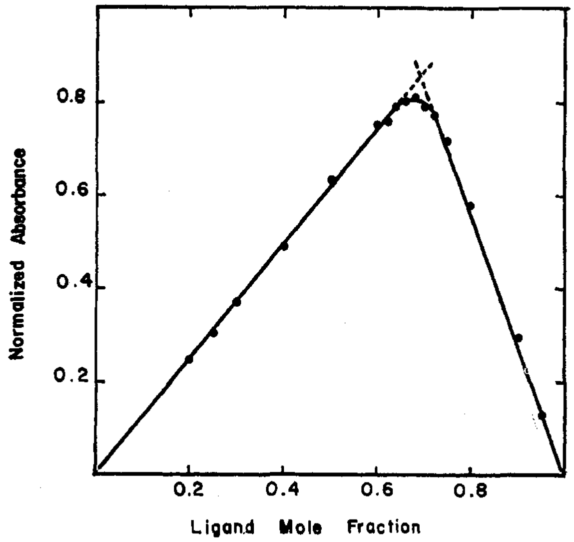


Figure 2.—Continuous-variations plot of ligand mole fraction *vs.* normalized absorbance. $k = 7.49 \times 10^{-5}$ $M$.

## Results

The solution spectrum of $Fe(TPTZ)_2^{2+}$ was reported by Diehl, *et al.*,[3] and an identical spectrum was observed by the present authors over the pH range 2.5–4.5. A shift in the wavelength of the main absorption peak and its shoulder peak was observed in the pH region 1.3–2.2. Figure 1 illustrates the linear pH dependence of the wavelength of both peaks. The wavelength shift is most likely the result of a statistical mixing of absorption peaks due to $Fe(TPTZ)_2^{2+}$ (593, 540 nm) and a second species (~615, 555 nm) presumed to be the protonated complex.

The normalized continuous-variations plot is presented in Figure 2. It closely resembles the unnormalized plot reported by Diehl, *et al.*[3] The linearity and peak position of the plot indicate that the absorbance is primarily due to $Fe(TPTZ)_2^{2+}$ and that the concentration of the mono complex, $Fe(TPTZ)^{2+}$, is negligibly small.

---

(11) K. Momoki, J. Sekino, H. Sato, and N. Yamaguchi, *Anal. Chem.*, **41**, 1286 (1969).

(12) F. H. Fraser and D. J. Macero, Third Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971, paper no. 16.

(13) W. Likussar and D. F. Boltz, *Anal. Chem.*, **43**, 1265 (1971).

(14) A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York, N. Y., 1963.

(15) J. N. Butler, "Ionic Equilibrium, a Mathematic Approach," Addison-Wesley, Reading, Mass., 1964.

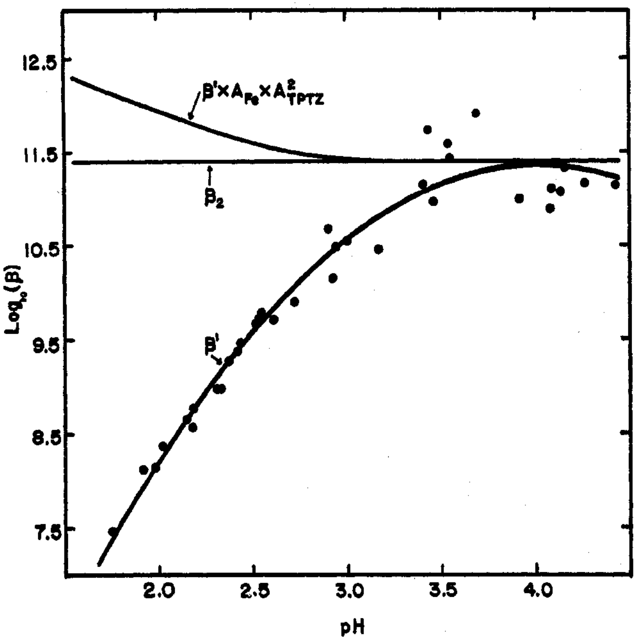


Figure 3.—The formation equilibrium constant of $Fe(TPTZ)_2{}^{2+}$. The points (●) correspond to experimentally determined values of $\beta'$. The solid curve labeled $\beta'$ is a second-order least-squares fit (rms deviation = 0.24). The curve $\beta' \times A_{Fe} \times A_{TPTZ}{}^2$ represents $\beta'$ compensated for ligand and metal ion hydrolysis only. The curve $\beta_2$ represents eq 2 with $\beta_{Fe(TPTZ)_2H^{3+}} = (2.5 \pm 1.1) \times 10^2$.

The conditional formation constant, $\beta'$, was determined from the normalized absorbances over a pH range 1.7–4.5 using eq 1 (derived by Likussar and

$$\beta' = [(m + n)/k]^{(m+n-1)} m^{-m} n^{-n} y(1 - y)^{-(m+n)} \qquad (1)$$

Boltz[13]), where $m = 1$ and $n = 2$ are the stoichiometric coefficients in the complex of the metal ion and the ligand, respectively, $k = 4.47 \times 10^{-5}\ M$ is the analytical concentration constant, and $y$ the normalized absorbance. The resulting curve is shown in Figure 3. Equation 1 assumes that $Fe(TPTZ)_2{}^{2+}$ is the only contributor to the measured absorbance and that its equilibrium concentration is predominant over that of the mono complex. The thermodynamic formation constant, $\beta_2$, for $Fe(TPTZ)_2{}^{2+}$ was determined by application of the coefficient expressions described by Ringbom[14] and Butler[15]

$$\beta_2 = \beta'(A_{Fe^{2+}} A_{TPTZ}{}^2)/A_{Fe(TPTZ)_2{}^{2+}} \qquad (2)$$

$$A_{Fe^{2+}} = [1 + \beta_{OH}(OH^-) + \beta_{2OH}(OH^-)^2] \qquad (3)$$

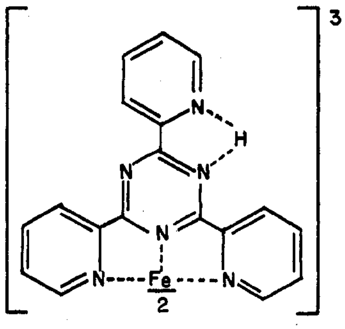
$$A_{TPTZ} = [1 + K_H(H^+) + (K_H K_{2H})(H^+)^2] \qquad (4)$$

$$A_{Fe(TPTZ)_2{}^{2+}} = [1 + \beta_{Fe(TPTZ)_2H^{3+}}(H^+)] \qquad (5)$$

where $\beta_{OH}$ and $\beta_{2OH}$ are the overall formation constants for the mono- and bis-hydroxide complexes of iron(II), respectively, $K_H$ and $K_{2H}$ are the stepwise protonation constants of TPTZ, and $\beta_{Fe(TPTZ)_2H^{3+}}$ is the formation constant for the protonated complex. A value of $\beta_{OH} = 1.26 \times 10^6$ was taken from Martell's[16] compilation of stability constants, and $\beta_{2OH} = 6.76 \times 10^{13}$ was approximated by the reciprocal of the $K_{sp}$. Inclusion of these values for $\beta_{OH}$ and $\beta_{2OH}$ in eq 3 had only a slight effect on the calculations over the pH range examined. The values for $K_H$ and $K_{2H}$ reported by Prasad and Peterson[10] were used in eq 4. The value of $K_H$ was numerically optimized to be $9.5 \times 10^2$, which is well within the reported error limits, $(8 \pm 5) \times 10^2$. A value of $(2.5 \pm 1.1) \times 10^2$ for $\beta_{Fe(TPTZ)_2H^{3+}}$ yielded a constant value for $\beta_2$ over the experimental pH range. Figure 3 shows the results of the equilibrium analysis. The solid $\beta'$ curve represents a second-order least-squares fit. The $\beta' \times A_{Fe} \times A_{TPTZ}{}^2$ curve represents eq 2 without inclusion of $\beta_{Fe(TPTZ)_2H^{3+}}$ in eq 5, and the $\beta_2$ curve represents $\beta_2$ when $\beta_{Fe(TPTZ)_2H^{3+}}$ equals $(2.5 \pm 1.1) \times 10^2$. Both curves were generated from the least-squares fit of $\beta'$. A value of $(2.8 \pm 1.2) \times 10^{11}$ was determined for $\beta_2$.

## Discussion

The spectral shift illustrated in Figure 1 was attributed to the formation of $Fe(TPTZ)_2H^{3+}$, since it was linearly dependent upon the pH. Furthermore, the shape of the absorption peak was essentially unchanged as it shifted in wavelength, which indicates that the absorption band responsible for the shift probably has a similar shape and that the new species is very similar in structure and symmetry to $Fe(TPTZ)_2{}^{2+}$. Note also that the ligand, TPTZ, when fully coordinated has a coordination-free pyridyl group, *i.e.*, a weak base, at the six position on the *s*-triazine ring. This suggests that a proton could easily become associated with the free pyridyl group. The formal charge of +2 on the complex ion would not favor this process; however, at high hydrogen ion concentrations the electrostatic repulsions could be overcome and lead to the formation of $Fe(TPTZ)_2H^{3+}$. Supporting this is the fact that a similar species, triaquo(2,6-di(2-pyridyl)-4-(pyridinium-2-yl bromide)-1,3,5-triazine)nickel(II) bromide monohydrate, $Ni(TPTZ)(H_2O)_3 \cdot HBr^{2+}$, was crystallographically observed by Barclay, *et al.*,[17] to have the hydrobromic acid molecule associated with the uncoordinated pyridyl group of TPTZ. Finally, the pH dependence of the conditional equilibrium constant could not be adequately rationalized without inclusion of the formation of $Fe(TPTZ)_2H^{3+}$.



$Fe(TPTZ)_2H^{3+}$

It was noted earlier that Pagenkopf and Margerum[8] discounted the formation of $Fe(TPTZ)_2H^{3+}$ on the basis of the observed dissociation rate constants for the dissociation of TPTZ from $Fe(TPTZ)_2{}^{2+}$. However, these investigators did observe that increased acid concentrations increased the rate of dissociation, relative to weakly acidic conditions, but that the limiting value

---

(16) A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

(17) G. A. Barclay, R. S. Vagg, and E. C. Watton, *Aust. J. Chem.*, **22**, 643 (1969).

of the acid dissociation rate was one-fifth the limiting value of the neutral dissociation rate. This they took to indicate that partial predissociation of one TPTZ moiety takes place before protonation of the complex. The evidence for a moderately stable $Fe(TPTZ)_2H^{3+}$ species may alter Pagenkopf and Margerum's conclusions. Our results indicate that a second process for the acid dissociation of $Fe(TPTZ)_2H^{3+}$ involving direct attack of $Fe(TPTZ)_2^{2+}$ by a proton should also be considered, although the observed evidence may only be a manifestation of the partially predissociated protonated complex proposed by Pagenkopf and Margerum.[8] No definitive conclusion can be drawn from the equilibrium analysis presented in this study; nevertheless, the formation of $Fe(TPTZ)_2H^{3+}$, partially dissociated or not, must be considered to rationalize the experimental data.

The value for $\beta_2 = (2.8 \pm 1.2) \times 10^{11}$ was determined by a technique which is independent of the molar absorbance. The molar absorbance is reported[3,9] to be 22,400 ± 200, and it may vary with the ligand concentration.[9] The two values for $\beta_2$ previously reported by Buchanan, *et al.*[9] ($\beta_2 = 1.75 \times 10^{10}$), and by Pagenkopf and Margerum[8] ($\beta_2 = (3.0 \pm 1.8) \times 10^{12}$) were determined with the aid of the molar absorbance. The use of the normalization of absorbances proposed by Momoki, *et al.*,[11] in the method described by Likussar and Boltz[13] for the determination of $\beta'$, and thus $\beta_2$, eliminates the molar absorbance from the problem, which enhances the reliability of the method presented in this study. Pagenkopf and Margerum[8] used a value of 21,600 for $\epsilon$ in their determination of $\beta_2$.

The reliability of the formation constant for $Fe(TPTZ)_2H^{3+}$, $(2.5 \pm 1.1) \times 10^2$, is dependent upon the assumptions concerning the equilibria present in the problem. Any contribution of $Fe(TPTZ)^{2+}$ to the formation equilibrium was dismissed because of the observed linearity of the Job plot (Figure 2); thus only $Fe(TPTZ)_2^{2+}$ was considered to contribute to the absorbance at 593 nm. The value of $K_{2H}$ is known,[10] $(6.58 \pm 0.01) \times 10^2$, but $K_H$ had to be numerically optimized. The value of $9.5 \times 10^2$ for $K_H$ was observed to give a well-behaved pH dependence of $\beta' \cdot A_{Fe}A_{TPTZ}^2$ (Figure 3). Variation of $K_H$ over its uncertainty limits had a negligible effect on $\beta_2$ at pH >3 and only a 10% effect at pH <2. Ultimately, the value for $\beta_{Fe(TPTZ)_2H^{3+}}$ was numerically found, and this value is highly dependent upon the value of $K_H$ for TPTZ used.

Absorbance measurements were hindered by ligand insolubility above pH 4.5. The reported solubility of TPTZ at pH 4.5 is $9.2 \times 10^{-5}$ mol/l.,[9] which is three times the concentration of TPTZ present in the solutions for the determination of $\beta'$. A marked decrease in the solubility of TPTZ must occur above a pH of 5, since $Fe(TPTZ)_2^{2+}$ solutions above this pH rapidly became turbid. Absorbance measurements made at a pH >4.5 were considered unreliable; therefore, the evaluation of $\beta'$ was restricted to the pH region between 1.5 and 4.5.

## Conclusion

The formation of a protonated complex ion, $Fe(TPTZ)_2H^{3+}$, was attributed to a spectral shift in the spectrum of $Fe(TPTZ)_2^{2+}$ at low pH. A value of $\beta_2 = (2.8 \pm 1.2) \times 10^{11}$ for $Fe(TPTZ)_2^{2+}$ was determined with the assumption that $\beta_{Fe(TPTZ)_2H^{3+}} = (2.5 \pm 1.1) \times 10^2$.

**Acknowledgment.**—We wish to thank the National Science Foundation for funds (NSF Grant No. GW-6639) to purchase chemicals for use on this project.

---

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

# Kinetics and Mechanisms of Some Substitution Reactions of Pentacyanoferrate(III) Complexes[1]

BY JAMES H. ESPENSON* AND STEPHEN G. WOLENUK, JR.

*Received January 27, 1972*

A procedure for the synthesis and purification of the monomeric complex $Fe(CN)_5H_2O^{2-}$ was devised. The following reactions were studied, with data at 25.0°, $\mu = 1.00\ M$, as indicated: (1) the equilibrium $Fe(CN)_5H_2O^{2-} + SCN^- = Fe(CN)_5SCN^{3-} + H_2O$ has $K = 257 \pm 15\ M^{-1}$ and a forward rate given by $\{a + b[H^+]^{-1}\}[Fe(CN)_5H_2O^{2-}][SCN^-]$, with $10^2a = 1.96 \pm 0.19\ M^{-1}\ sec^{-1}$ and $10^3b = 5.2 \pm 0.3\ sec^{-1}$; (2) the reaction $Fe(CN)_5SCN^{3-} + OH^- = Fe(CN)_5OH^{3-} + SCN^-$ proceeds quantitatively to the right at $[OH^-]/[SCN^-] > 0.2$ with a pseudo-first-order rate constant given by $A + B[OH^-]/\{[OH^-] + C[SCN^-]\}$ (the values at 25°, $\mu = 1.00\ M$, are $10^3A = 2.78 \pm 0.05\ M^{-1}\ sec^{-1}$, $10^2B = 1.32 \pm 0.09\ M^{-1}\ sec^{-1}$, and $C = 3.1 \pm 0.4$); (3) the reaction of the dimer $Fe_2(CN)_{10}^{4-}$ with $SCN^-$ occurs in two stages

$$Fe_2(CN)_{10}^{4-} \xrightarrow{k_1\ [SCN^-]} [Fe_2(CN)_{10}SCN^{5-}] \xrightarrow{k_2\ [SCN^-]} 2Fe(CN)_5SCN^{3-}$$

with $k_1 = 0.010$ and $k_2 \cong 10^{-4}\ M^{-1}\ sec^{-1}$. The kinetic data for all of these reactions are interpreted in terms of proposed reaction mechanisms.

## Introduction

At the beginning of this century Hofmann[2] prepared complexes of the empirical formula $Na_3Fe(CN)_5(H_2O)_x$ and $Na_2Fe(CN)_5(H_2O)_y$. Subsequent work on these supposed "aquo" complexes, largely by Emschwiller and coworkers,[3] has established the dimeric

---

[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3198. (b) Based on the M.S. thesis of S. G. W., Jr., Iowa State University, Dec 1971.

[2] K. Hofmann, *Ann. Chem.*, **312**, 1 (1900).

[3] (a) G. Emschwiller, *C. R. Acad. Sci.*, **247**, 1115 (1958); (b) *C. R. Acad. Sci., Ser. C*, **265**, 281 (1967); (c) *ibid.*, **268**, 692 (1969); (d) G. Emschwiller and C. K. Jørgensen, *Chem. Phys. Lett.*, **5**, 561 (1970).