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# Electrochemistry and Hydrolysis Kinetics of the 2,2′-Bipyridine Complexes of Iron(III) and Iron(II)

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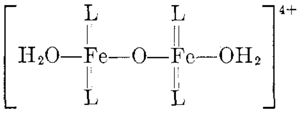
The electrochemistry and hydrolysis kinetics of the 2,2′-bipyridine (bipy) complexes of Fe(III) and Fe(II) have been studied by chronopotentiometry and cyclic voltammetry. The reduction of the brown, oxo-bridged $Fe_2(bipy)_4O(H_2O)_2^{4+}$ complex at prereduced gold and platinum electrodes is a one-electron, diffusion-controlled, irreversible process with an $\alpha n_a$ value of 0.46. Galvanostatic studies establish that the value of $E_{t=0}$ for the complex shifts with pH and bipy concentration. The reduction product gives a reverse chronopotentiometric wave (at a potential 0.66 V anodic from the forward wave) which is due to the oxidation of the red $Fe(bipy)_3^{2+}$ complex. The blue $Fe(bipy)_3^{3+}$ complex is reduced at platinum and gold electrodes by a reversible, one-electron, diffusion-controlled process with a formal potential of +0.79 V *vs.* sce which is independent of pH (pH 2–10) and of the concentration of bipy. The hydrolysis of $Fe(bipy)_3^{3+}$ to $Fe_2(bipy)_4O(H_2O)_2^{4+}$ is first order in $Fe(bipy)_3^{3+}$ and first order in base. The rate constants for three bases are: $k_{H_2O}[H_2O] = 8.4 \times 10^{-5}$ sec$^{-1}$; $k_{bipy} = 4.1 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$; $k_{OH^-} = 4.3 \times 10^5$ l. mol$^{-1}$ sec$^{-1}$. A mechanism consistent with the experimental data is proposed for the hydrolysis. The equilibrium constant for the hydrolysis reaction has an approximate value of $6 \times 10^{-9}$ at low concentrations of bipy.

Although the 2,2′-bipyridine (bipy) complexes of Fe(III) and Fe(II) have been studied by several groups,[1–6] the details of the electrochemical reduction of the brown Fe(III)–bipy complex and the nature of the hydrolysis of the blue Fe(III)–bipy complex have not been established. The brown complex (obtained by direct addition of Fe(III) to a bipy solution) is believed to be a binuclear species with an oxygen bridge[1,2]



$$\left[\begin{array}{ccccc} & L & & L & \\ & | & & \| & \\ H_2O- & Fe & -O- & Fe & -OH_2 \\ & | & & \| & \\ & L & & L & \end{array}\right]^{4+}$$

where L is bipy. The blue Fe(III) complex, $Fe(bipy)_3^{3+}$, is produced by chemical or electrochemical oxidation of the red Fe(II) complex, $Fe(bipy)_3^{2+}$. Although the blue complex is relatively stable in strong acids, with dilute acids it hydrolyzes to free Fe(III) and protonated bipy.[3–6] In solutions of higher pH the blue complex is hydrolyzed to the brown complex.[3,6]

The electrochemical behavior of the bipy complexes of Fe(II) and Fe(III) has been studied by voltammetry with a platinum electrode.[6] The authors concluded that the $Fe(bipy)_3^{2+} \rightleftarrows Fe(bipy)_3^{3+} + e^-$ couple is reversible and that the electrochemical reduction of the oxo-bridged $Fe_2(bipy)_4O(H_2O)_2^{4+}$ species is irreversible but diffusion controlled with the voltammetric wave preceded by a kinetically controlled prewave.

Several reactions of the bipy complexes of Fe(III) and Fe(II) complicate their study. For example, all three complexes dissociate to free iron and protonated bipy in dilute solutions of strong acids. Above pH 6 the $Fe_2(bipy)_4O(H_2O)_2^{4+}$ species precipitates as $Fe_2O_3 \cdot xH_2O$, and above pH 5 uncomplexed bipy tends to precipitate. In addition, above pH 7 $OH^-$ reduces $Fe(bipy)_3^{3+}$ to $Fe(bipy)_3^{2+}$, and both the blue and brown bipy complexes of Fe(III) can be photoreduced to the red $Fe(bipy)_3^{2+}$ complex.[3]

The present paper summarizes the results of a detailed electrochemical study of the iron–bipy complexes; a mechanism for the hydrolysis of the $Fe(bipy)_3^{3+}$ complex to the brown, oxo-bridged complex, $Fe_2(bipy)_4O(H_2O)_2^{4+}$, is proposed.

## Experimental Section

The electrochemical measurements were made with a versatile instrument constructed from Philbrick operational amplifiers following the design of DeFord.[7] In addition, a Hewlett-Packard Model 202A low-frequency function generator and a Tektronix Model 564 oscilloscope were used for fast-scan triangular-wave cyclic voltammetry. A three-electrode assembly in a Leeds and Northrup 100-ml coulometry cell was used for all electrochemical studies; the cell was covered with aluminum foil to exclude light. pH measurements were made with a Corning Model 12 pH meter. Rapid conversion of red $Fe(bipy)_3^{2+}$ to blue $Fe(bipy)_3^{3+}$ was accomplished with a Hewlett-Packard dc power supply connected to a Pt gauze anode and a Pt flag cathode. A thermostated water bath was used to control temperatures. The reference electrode consisted of an AgCl-coated Ag wire in a solution of 0.4 *F* KCl contained in a 9-cm length of borosilicate glass tubing with a small ball of soft glass sealed in one end to give a cracked tip; its potential was 0.000 V *vs.* sce. The auxiliary electrode was a Pt flag. Three working electrodes were employed: a gold cylinder inlayed into polyethylene tubing, a Beckman platinum-inlay electrode, and a mercury electrode prepared by abrading a Beckman Pt-inlay electrode with

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(1) W. M. Reiff, W. A. Baker, Jr., and N. E. Erickson, *J. Am. Chem. Soc.*, **90**, 4794 (1968).

(2) G. Anderegg, *Helv. Chim. Acta*, **45**, 1643 (1962).

(3) E. M. Gusenius, University Microfilms, Ann Arbor, Mich, Order No. 63-6795, 121 pp; *Dissertation Abstr.*, **24**, 1386 (1963).

(4) A. F. Richards, J. H. Ridd, and M. L. Tobe, *Chem. Ind.* (London), **43**, 1726 (1963).

(5) R. K. Murmann and E. A. Healy, *J. Am. Chem. Soc.*, **83**, 2092 (1961).

(6) F. Pantani and G. Ciantelli, *J. Electroanal. Chem.*, **14**, 423 (1967).

(7) D. D. DeFord, private communication; presented at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958.

carborundum paper in a mercury pool until a uniform coverage of mercury was obtained. The areas of the Au and Pt electrodes were determined electrochemically from the reduction of $K_3Fe(CN)_6$ in 0.5 $F$ KCl; their respective areas were 0.192 and 0.237 $cm^2$.

2,2'-Bipyridine (bipy) was obtained from Columbia Organic Chemicals Co., Inc., and from Aldrich Chemical Co., Inc. Iron(III) was derived from $Fe(NO_3)_3 \cdot 9H_2O$, and iron(II) was produced by electrolyzing Fe(III) solutions at a Pt-gauze electrode. Solutions were degassed with prepurified $N_2$ obtained from the Matheson Co. The pH of the iron–bipy solutions was adjusted with $HNO_3$ and KOH.

The $pK_a$ of protonated bipy in 1.0 $F$ $KNO_3$ was determined by dissolving bipy in a slight excess of $HNO_3$ and then titrating the mixture of $HNO_3$ and protonated bipy with 0.1 $F$ NaOH in 1.0 $F$ $KNO_3$. Assuming that the $pK_a$ value equals the pH when protonated bipy is 50% titrated, a value of 4.57 ± 0.04 was obtained; a value of 4.44 has been reported for the $pK_a$ in 0.1 $F$ $KNO_3$.[8,9] Because of hydrolysis the diffusion coefficient of $Fe(bipy)_3{}^{3+}$ could not be determined accurately; it was assumed to be equal to that for $Fe(bipy)_3{}^{2+}$.

## Results

**$Fe_2(bipy)_4O(H_2O)_2$.**—Chronopotentiometric reduction of the brown, oxo-bridged species at prereduced gold and platinum electrodes gives well-defined waves in 1.0 $F$ $KNO_3$ solutions between pH 2 and 6 (Figure 1). At pH 4.0 and $7.71 \times 10^{-3}$ $M$ bipy the quarter-wave potential, $E_{1/4}$, is +0.07 V *vs.* sce. A reverse chronopotentiometric wave is observed with a value for $E_{0.22}$ of +0.73 V *vs.* sce; this wave is due to the oxidation of red $Fe(bipy)_3{}^{2+}$. Fast-scan triangular-wave voltammetry (up to 20 V/sec) fails to indicate the presence of any other Fe(II) species. Reduction of $Fe_2(bipy)_4O(H_2O)_2{}^{4+}$ by chronopotentiometry indicates a diffusion-controlled process for currents from 18 to 400 $\mu$A; the value of $i\tau^{1/2}/AC^0$ is 192 ± 7 A $sec^{1/2}$ cm $mol^{-1}$, where $i$ is the current, $\tau$ the transition time, $A$ the electrode area, and $C^0$ the bulk concentration of the electroactive species.

The chronopotentiometric data also indicate that the reduction of $Fe_2(bipy)_4O(H_2O)_2{}^{4+}$ at gold and platinum electrodes is an irreversible process that is controlled by semiinfinite linear diffusion. The relationship between potential and time (at constant current) for such a system is given by[10]

$$E_t = \frac{0.059}{\alpha n_a} \log \frac{nFAC^0k^0_{f,h}}{i} + \frac{0.059}{\alpha n_a} \log \left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right] \quad (1)$$

where $E_t$ is the potential of the working electrode *vs.* nhe, $\alpha$ the transfer coefficient, $n_a$ the number of electrons in the rate-determining step, $A$ the electrode area, $k^0_{f,h}$ the heterogeneous rate constant for the reduction reaction, $i$ the current, $C^0$ the bulk concentration of the electroactive species, $F$ the Faraday constant, $\tau$ the transition time, and $t$ the time of electrolysis. This equation can be used to evaluate $\alpha n_a$ by plotting either $E_t$ *vs.* $\log [1 - (t/\tau)^{1/2}]$ or $E_{t=0}$ *vs.* $-\log i$. Such plots give linear curves for the reduction of $Fe_2(bipy)_4O(H_2O)_2{}^{4+}$ at a prereduced gold electrode; the average value obtained for $\alpha n_a$ is 0.46 ± 0.06. This value implies that the rate-determining electron-transfer reaction is a one-electron process. The value of $E_{t=0}$ shifts about −0.02 V per pH unit from pH 3.0 to pH 6.0; it shifts about +0.03 V per tenfold increase in bipy concentration from $5 \times 10^{-3}$ to $5 \times 10^{-2}$ $M$ bipy.

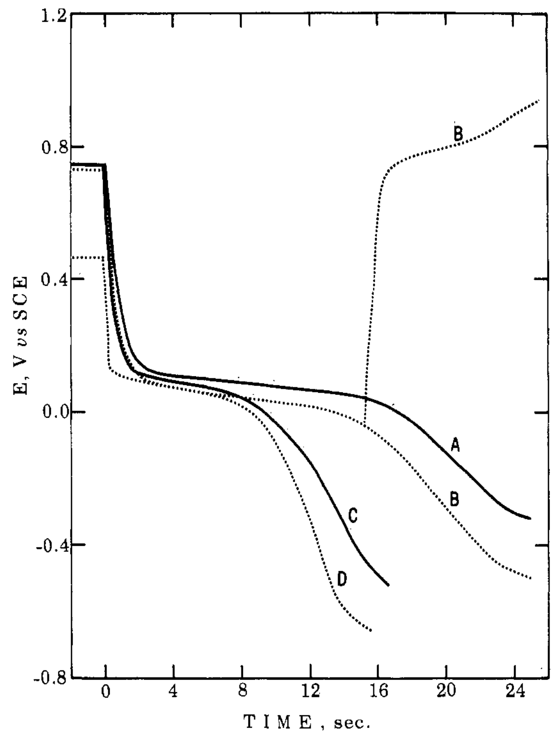

Figure 1.—Chronopotentiograms of $5.0 \times 10^{-4}$ $M$ oxo-bridged $Fe_2(bipy)_4O(H_2O)_2{}^{4+}$ at a gold electrode in 1.0 $F$ $KNO_3$: A, $7.71 \times 10^{-3}$ $M$ bipy, pH 3.0, 8 $\mu$A; B, $7.71 \times 10^{-3}$ $M$ bipy, pH 4.0, 8 $\mu$A; C, pH 4.7, $3.92 \times 10^{-2}$ $M$ bipy, 10 $\mu$A; D, pH 5.0, $5.0 \times 10^{-3}$ $M$ bipy, 10 $\mu$A.

**$Fe(bipy)_3{}^{3+}$.**—The blue iron(III) complex gives well-developed chronopotentiometric and voltammetric reduction waves at gold and platinum electrodes following electrochemical oxidation of the red complex, $Fe(bipy)_3{}^{2+}$. The latter can be formed by the electrochemical reduction of the brown oxo-bridged iron(III) complex (Figure 2). The reversible $Fe(bipy)_3{}^{3+}$–$Fe(bipy)_3{}^{2+}$ couple has a formal potential, $E'$, of +0.79 V *vs.* sce in 1.0 $F$ $KNO_3$, which is independent of pH (from pH 2 to pH 10) and of bipy concentration (from 0.0 to 0.1 $M$).

The hydrolysis of the blue complex to the brown, oxo-bridged complex in 2.0 $F$ $KNO_3$, for acidities between pH 2 and 6, can be followed by monitoring the concentration of the blue complex chronopotentiometrically. For a diffusion-controlled chronopotentiometric process the relationship between the transition time and the bulk concentration of the electroactive species is given by the Sand equation[11]

$$i\tau^{1/2} = \pi^{1/2}nFAD^{1/2}C^0/2 \quad (2)$$

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[8] M. Yasuda, K. Sane, and K. Yamasaki, *J. Phys. Chem.*, **60**, 1667 (1956).

[9] K. Yamasaki and M. Yasuda, *J. Am. Chem. Soc.*, **78**, 1324 (1956).

[10] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p 187.

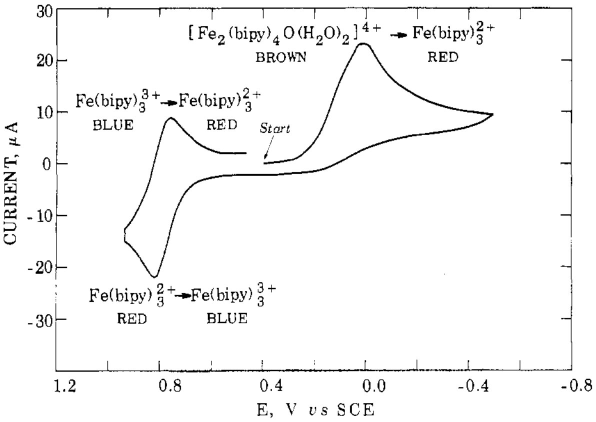

Figure 2.—Cyclic voltammogram of $5.0 \times 10^{-4}$ *M* $Fe_2(bipy)_4O(H_2O)_2^{4+}$ at a gold electrode. Solution: 1.0 *F* $KNO_3$, $7.9 \times 10^{-5}$ *M* bipy, and pH 3.0. Scan rate, 0.1 V/sec.

where $i$ is the current, $\tau$ the transition time, $n$ the number of electrons in the over-all process, $F$ the Faraday constant, $A$ the area of the electrode, $D$ the diffusion coefficient of the electroactive species, and $C^0$ the bulk concentration of the electroactive species. Hydrolysis studies of $Fe(bipy)_3^{3+}$ confirm that $i\tau^{1/2}$ for the reduction wave of the blue complex decreases with time; in contrast $i\tau^{1/2}$ for the reduction wave of the brown complex increases with time. Thus, eq 2 can be used to evaluate the concentrations of $Fe(bipy)_3^{3+}$ and $Fe_2(bipy)_4O(H_2O)^{4+}$.

The data establish that the hydrolysis of blue $Fe(bipy)_3^{3+}$ to brown $Fe_2(bipy)_4O(H_2O)_2^{4+}$ between pH 2 and 6 is first order in $Fe(bipy)_3^{3+}$ and first order in any base which is present, *e.g.*, $H_2O$, $OH^-$, and bipy. Plots for a pseudo-first-order reaction yield straight lines whose slopes depend upon the pH and upon the concentration of unprotonated bipy (Figure 3). Oxygen does not have a measurable effect on the rate of hydrolysis. For some conditions the equilibrium concentration of $Fe(bipy)_3^{3+}$ is not negligible, which has required that the observed concentration be corrected before plotting. These results indicate that the hydrolysis of $Fe(bipy)_3^{3+}$ can follow as many paths as there are bases present. By formulating and solving simultaneous equations, the values for the rate constants can be evaluated for the three bases present: $k_{H_2O}[H_2O] = 8.4 \times 10^{-4}$ sec$^{-1}$; $k_{bipy} = 4.1 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$; $k_{OH^-} = 4.3 \times 10^5$ l. mol$^{-1}$ sec$^{-1}$ at $25.0 \pm 0.1°$.

The hydrolysis of $Fe(bipy)_3^{3+}$ has been studied at 15.0, 20.0, and 25.0° for an average pOH of 9.25 and unprotonated bipy concentration of $3.0 \times 10^{-2}$ *M*. An Arrhenius plot yields a straight line which indicates an activation energy, $E_a$, of 21.6 kcal mol$^{-1}$ and a $\Delta S^{\ddagger}$ value of $-1.5$ eu.

At low values of pH, or at high concentrations of bipy, or both, the equilibrium concentration of blue $Fe(bipy)_3^{3+}$ in 2.0 *F* $KNO_3$ is sufficiently large (>0.3 m*M*) to be measured accurately by chronopotentiometry. This permits the value of the equilibrium constant for the reaction

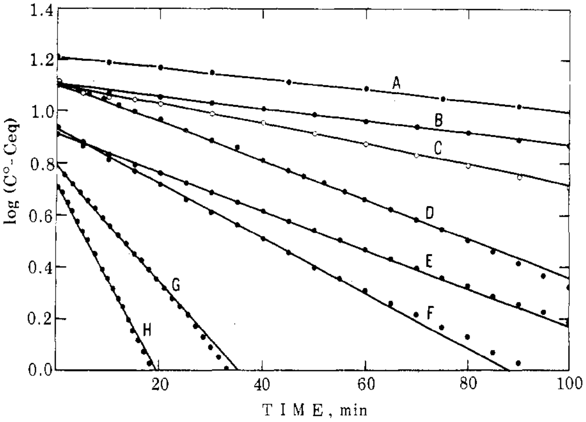

Figure 3.—Kinetics of hydrolysis for $Fe(bipy)_3^{3+}$ in 2.0 *F* $KNO_3$ at 25.0°: A, pH 2.08, $7.1 \times 10^{-5}$ *M* bipy; B, pH 3.23, $3.85 \times 10^{-4}$ *M* bipy; C, pH 3.29, $1.27 \times 10^{-2}$ *M* bipy; D, pH 4.40, $2.29 \times 10^{-3}$ *M* bipy; E, pH 3.22, $5.35 \times 10^{-2}$ *M* bipy; F, pH 3.15, $7.72 \times 10^{-2}$ *M* bipy; G, pH 5.23, $8.06 \times 10^{-3}$ *M* bipy; H, pH 5.48, $9.06 \times 10^{-3}$ *M* bipy. $C^0$ is the concentration of $Fe(bipy)_3^{3+}$ (m*M*) (monitored by chronopotentiometry); $C_{eq}$ is the equilibrium concentration.

$$2Fe(bipy)_3^{3+} + 3H_2O \rightleftarrows Fe_2(bipy)_4O(H_2O)_2^{4+} + 2H^+ + 2bipy \ (K_{eq}) \qquad (3)$$

to be calculated. Although the value of $pK_{eq}$ varies with bipy concentration because of competing reactions, it has an approximate value of 8.2 at low concentrations of bipy. Equilibrium can be approached from the opposite direction, *i.e.*, by starting with only oxo-bridged $Fe_2(bipy)_4O(H_2O)_2^{4+}$ in the solution. Thus, when a solution of 0.11 *M* bipy in 1.0 *F* $KNO_3$ at pH 3.53 is made 10 m*M* in $Fe_2(bipy)_4O(H_2O)_2^{4+}$ with $Fe(NO_3)_3$, the concentration of blue $Fe(bipy)_3^{3+}$ increases to an equilibrium value which is in agreement with the values obtained by the hydrolysis of $Fe(bipy)_3^{3+}$.

The diffusion coefficients for $Fe_2(bipy)_4O(H_2O)_2^{4+}$ (0.01 *M* bipy and pH 5.00) and $Fe(bipy)_3^{2+}$ (0.03 *M* bipy and pH 3.00) in 1.0 *F* $KNO_3$ are $4.85 \times 10^{-6}$ and $5.10 \times 10^{-6}$ cm$^2$ sec$^{-1}$, respectively, on the basis of the chronopotentiometric data.

Values for the simple heterogeneous electrochemical rate constant, $k_{s,h}$, the diffusion coefficients of the oxidized and reduced species, $D_o$ and $D_r$, and the formal electrode potential, $E'$, for the $Fe(bipy)_3^{3+}$–$Fe(bipy)_3^{2+}$ couple are summarized in Table I together with the values for several other Fe(II)–Fe(III) complexes. The rate constants have been evaluated by triangular-wave cyclic voltammetry using the Nicholson equation[12]

$$k_{s,h} = \frac{\psi(\pi n D_o \nu/0.0257)^{1/2}}{(D_o/D_r)^{\alpha/2}} \qquad (4)$$

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(11) See ref 10, p 194.

(12) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).

TABLE I

ELECTROCHEMICAL PARAMETERS FOR SEVERAL IRON(II) AND IRON(III) COMPLEXES

| System (all contain 2 m*F* Fe) | Electrode | E′, V *vs.* sce | $10^6 D_o$, cm² sec⁻¹ | $10^6 D_r$, cm² sec⁻¹ | Log $k_{s,h}$ Exptl | Log $k_{s,h}$ Lit.[a] |
|---|---|---|---|---|---|---|
| $1.0 \times 10^{-2}$ *F* bipy, 1.0 *F* $KNO_3$, pH 2.0 | Pt | +0.79 | . . . | 4.57 | −1.36 | . . . |
| $1.0 \times 10^{-2}$ *F* *o*-phenanthroline, 1.0 *F* $Na_2SO_4$, pH 2.0 | Pt | +0.83 | . . . | 5.93 | −1.17 | . . . |
| 1.0 *F* $HClO_4$ | Pt | +0.46 | 7.51 | 8.05 | −2.16 | −2.30 to −2.66 |
| $1.2 \times 10^{-2}$ *F* KCN, 1.0 *F* KCl | Pt | +0.21 | 8.00 | 7.20 | −1.06 | −1.05 to −1.28 |
| 1.0 *F* HCl | Au | +0.42 | 6.60 | 7.29 | −1.80 | . . . |
| 1.0 *F* NaSCN, pH 3.0 | Pt | +0.32 | . . . | . . . | −2.35 | . . . |
| 0.2 *F* $Na_2H_2EDTA$, 0.8 *F* $NaClO_4$, pH 4.4 | Hg | −0.13 | 4.15 | 4.35 | −1.33 | . . . |

[a] N. Tanaka and R. Jamamuski, *Electrochim. Acta*, 9, 963 (1964).

where $\psi$ is a function of peak separation and $n$, $n$ is the number of electrons involved in the redox system, $\nu$ is the scan rate, $\alpha$ is the transfer coefficient, and $D_o$ and $D_r$ are the diffusion coefficients for the oxidized and reduced species, respectively.

## Discussion and Conclusions

The data indicate that the electrochemical reduction of oxo-bridged $Fe_2(bipy)_4O(H_2O)_2^{4+}$ at prereduced platinum and gold electrodes is a one-electron, diffusion-controlled process. Because the value of $E_{t=0}$ shifts about −0.02 V per pH unit from pH 3.0 to 6.0 and about +0.03 V per tenfold increase in bipy concentration from $5 \times 10^{-3}$ to $5 \times 10^{-2}$ *M*, the rate-determining step for the reduction of $Fe_2(bipy)_4O(H_2O)_2^{4+}$ does not have a simple integral dependence on $H^+$ or on bipy. A mechanism consistent with the data can be written that has a rate-determining step which does not involve either $H^+$ or bipy

$$Fe_2(bipy)_4O(H_2O)_2^{4+} + e^- \rightarrow Fe_2(bipy)_4O(H_2O)_2^{3+} \quad \text{slow} \quad (5)$$

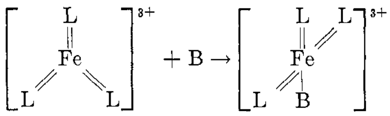
$$Fe_2(bipy)_4O(H_2O)_2^{3+} + Hbipy^+ \rightarrow Fe(bipy)_3^{2+} + H_2O + Fe(bipy)_2OH(H_2O)^{2+} \quad \text{fast} \quad (6)$$

$$2Fe(bipy)_2OH(H_2O)^{2+} \rightarrow Fe_2(bipy)_4O(H_2O)_2^{4+} + H_2O \quad \text{fast} \quad (7)$$

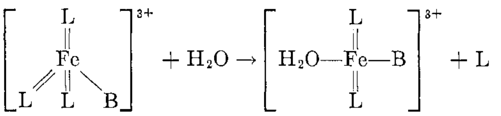
The blue $Fe(bipy)_3^{3+}$ complex is reduced reversibly to the red $Fe(bipy)_3^{3+}$ complex by a one-electron, diffusion-controlled process at gold and platinum electrodes. However, the system is complicated because $Fe(bipy)_3^{3+}$ hydrolyzes to $Fe(bipy)_4O(H_2O)_2^{4+}$. Kinetic studies indicate that the process is first order in $Fe(bipy)_3^{3+}$ and first order in any base which is present. Thus, a reasonable rate law is

$$\frac{-dC^0}{dt} = C^0 \Sigma_i k_i [B_i] \quad (8)$$

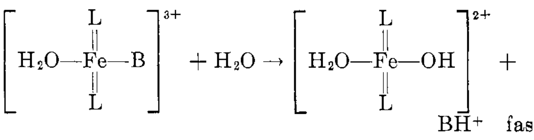
where $C^0$ is the concentration of $Fe(bipy)_3^{3+}$ at any time $t$, and $k_i$ is the second-order rate constant for the $i$th base, $B_i$. On the basis of this rate expression and the observed data, a plausible mechanism can be proposed



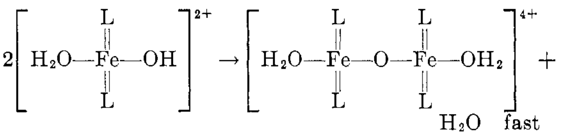
slow (9)



fast (10)



fast (11)



fast (12)

Equation 11 represents a hydrolysis step if B is not $OH^-$. At high pH values hydrolysis to $Fe_2O_3 \cdot xH_2O$ would compete with the reaction represented by eq 11.

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