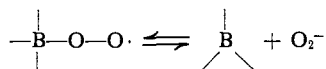


The presence of three distinct paramagnetic oxygen-containing species in the thermally reacted EMPB samples, plus a relatively unstable fourth species observed only in irradiated samples, invites the question: Are these species in equilibrium with each other or are they formed in separate, competitive paths? This question can be partially answered from the data on irradiated samples. It was found<sup>11,12</sup> that during irradiation of various EMPB samples the ratio of number of Z centers to number of X centers remained essentially constant after an initial period wherein the X centers were observed but no significant Z centers. Therefore, it seems possible that the chemical species giving rise to these two signals are in some type of equilibrium (or steady state) when the reaction is "turned on," *i.e.*, when the irradiation is being carried out or when the material is maintained at a temperature sufficient for the reaction to proceed thermally. It would not be surprising to find that the equilibrium



is set up. Addition of oxygen bases to three-coordinate borons and the reverse process are known to be facile.<sup>40</sup> Similarly, the ratio of Y to Z was constant as both

(40) R. P. Bell, J. O. Edwards, and R. B. Jones "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 4.

increased during the course of the irradiation. On the other hand, the intensity of the Z' resonance first increased and then decreased with length of irradiation, suggesting that this signal is due to a precursor for the species which gives the other signals.<sup>11,12</sup>

The unusual nature of the EMPB preparations has led us to experiments which have in turn given a variety of specific and interesting results, as, for example, the esr and isotope data. We feel, moreover, that these systems give results and allow conclusions which may have broader generality and which may be applied to other systems.

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## The Oxidation of Tris(1,10-phenanthroline)iron(II) Ion by Chlorate and Chlorite Ions and Chlorine Dioxide<sup>1a</sup>

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*Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. Received August 9, 1968*

**Abstract:** The reactions of chlorate and chlorite ions and chlorine dioxide with  $\text{Fe}(\text{phen})_3^{2+}$  have been studied. In the case of  $\text{ClO}_2^-$ , the rate of the reaction is controlled by the first dissociation step of  $\text{Fe}(\text{phen})_3^{2+}$  and the iron(III) product is a dimeric species. Chlorine dioxide reacts *via* an outer-sphere path, since the iron(III) product is the monomeric species  $\text{Fe}(\text{phen})_3^{3+}$ . Chlorate ion is unreactive with  $\text{Fe}(\text{phen})_3^{2+}$ . The results are compared with those of other investigations which involve the chlorine oxidants and the aquated  $\text{Fe}^{2+}$  ion and also other metal ions and complexes. A general classification of  $\text{Fe}(\text{phen})_3^{2+}$  redox reactions is suggested.

It has been suggested<sup>2</sup> that the reactions between the chlorine oxidants and certain metal ions proceed *via* an inner-sphere path. The chlorine oxidants can be reduced in both one- and two-electron steps. For example, in the reduction of chlorate ion to chloride ion in acid solution, chlorine dioxide, chlorous acid, hypochlorous acid, and chlorine are possible inter-

mediates. These intermediates can either interact with one another or they can, in turn, be reduced ultimately to chloride ion if the rates of their further reduction are faster than the rates of their self-interaction.

The reaction between chlorine and tris(1,10-phenanthroline)iron(II) ion<sup>3</sup> is postulated<sup>4</sup> to proceed *via* an outer-sphere path with the formation of a chlorine radical,  $\text{Cl}_2^-$ , as a reactive intermediate.

The purpose of this paper is to present our results of the reduction of the other chlorine oxidants by  $\text{Fe}(\text{phen})_3^{2+}$ .

(1) (a) Part of the thesis presented by B. Z. Shkhashiri to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1967; (b) Postdoctoral Research Associate in Chemistry, University of Illinois, Urbana, Ill., 61801; (c) Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.  
(2) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 562 (1966).

(3) Hereafter  $\text{Fe}(\text{phen})_3^{2+}$ .

(4) B. Z. Shkhashiri and G. Gordon, *Inorg. Chem.*, **7**, 2454 (1968).

**Table I.** Typical Change in Absorbance as a Function of Time

Time, sec	$A_{\text{measd}}$	$A_{\text{compd}}^a$
300	1.230	1.232
600	1.105	1.104
900	0.991	0.989
1200	0.887	0.886
1500	0.791	0.793
1800	0.710	0.712
2100	0.635	0.637
2400	0.569	0.570
2700	0.510	0.511
3000	0.458	0.458
3300	0.410	0.410
3600	0.367	0.367
3900	0.330	0.329
4200	0.295	0.295
5 hr	0.0	0.0

<sup>a</sup> Computed  $A_0 = 1.326$ ;  $k = 3.67 \pm 0.005 \times 10^{-4} \text{ sec}^{-1}$  (the uncertainty corresponds to one standard deviation).

**Table II.** Rate of Dissociation of  $\text{Fe}(\text{phen})_3^{2+}$ 

$A_0^a$	$[\text{H}^+]_0, M$	$k \times 10^5, \text{sec}^{-1}$
0.576 <sup>b</sup>	2.0	7.55
1.325	0.5	7.30
0.267	0.1	7.50
1.325	0.001	6.92
1.385 <sup>c</sup>	0.01	35.3 <sup>e</sup>
1.557 <sup>d</sup>	0.01	37.5 <sup>e</sup>
0.850	0.001	38.0 <sup>e</sup>

<sup>a</sup> Initial absorbance at 5100 Å in 0.5-cm cell at 25°; ionic strength maintained at 1.0 M with either  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$  or  $\text{H}_2\text{SO}_4$ . <sup>b</sup> 2.0 M ionic strength. <sup>c</sup> 0.1 M ionic strength. <sup>d</sup> 0.4 M ionic strength. <sup>e</sup> 35°.

**Table III.** Rate of Dissociation of  $\text{Fe}(\text{phen})_3^{2+}$ 

$A_0^a$	$[\text{H}^+]_0, M$	$k \times 10^4, \text{sec}^{-1}$	$I, M$
0.868	0.01	9.65 <sup>b</sup>	0.1
0.749	0.01	7.14 <sup>b</sup>	0.4
1.807	0.1	6.55 <sup>b</sup>	0.1
0.320	4.0	<0.01	4.0
0.302	6.0	<0.01	6.0
0.575	0.01	0.140 <sup>c</sup>	0.4
1.150	0.01	0.141 <sup>c</sup>	0.4

<sup>a</sup> Initial absorbance at 5900 Å in 10.0-cm cell;  $\text{Fe}(\text{phen})_3^{3+}$  obtained by adding  $\text{PbO}_2$  and dilute  $\text{H}_2\text{SO}_4$  to  $\text{Fe}(\text{phen})_3^{2+}$  solutions followed by filtration; these readings were taken about 10 min after the addition of  $\text{PbO}_2$ . The ionic strength maintained by means of  $\text{H}_2\text{SO}_4$  and/or potassium sulfate. <sup>b</sup> 35°. <sup>c</sup> 25°.

## Experimental Section

**Chemicals.** Standard solutions of sodium chlorate were prepared by dissolving the solid in water. Fresh solutions of sodium chlorite were prepared and analyzed iodometrically<sup>5</sup> prior to each kinetic experiment. Chlorine dioxide<sup>6,6</sup> and  $\text{Fe}(\text{phen})_3^{2+}$  solutions<sup>4</sup> were prepared and analyzed by standard procedures.

**Procedure.** For most of the kinetic experiments, the ionic strength was adjusted to  $1.00 \pm 0.03 M$  with sodium sulfate or sodium nitrate. The experiments consisted of mixing a solution of  $\text{Fe}(\text{phen})_3^{2+}$  with a solution which contained the oxidant and the desired concentrations of sodium sulfate and sulfuric acid.

In a typical experiment 2 ml of  $5 \times 10^{-4} M$  sulfuric acid solution and 2 ml of  $2.0 \times 10^{-2} M$  sodium chlorite solution were added to 6 ml of 1.0 M sodium sulfate solution in a small flask. The flask

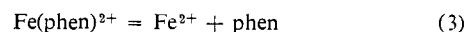
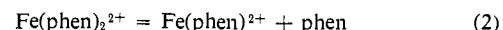
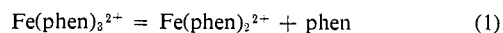
was placed in a 35.0° bath. After 10 min, 2 ml of this solution was withdrawn in a pipet and mixed thoroughly with an equal volume of  $\text{Fe}(\text{phen})_3^{2+}$  solution in a small beaker. This reaction mixture was quickly transferred into a 0.5-cm cell which was placed in the sample compartment of a Cary 14 recording spectrophotometer. The reference compartment contained a 0.5-cm cell filled with water. The concentrations upon mixing were:  $[\text{ClO}_2^-] = 2 \times 10^{-3} M$ ,  $[\text{H}_2\text{SO}_4] = 5 \times 10^{-5} M$ ,  $[\text{Na}_2\text{SO}_4] = 0.333 M$ ,  $[\text{Fe}(\text{phen})_3^{2+}] = 2.39 \times 10^{-4} M$ . The ionic strength was 1.00 M and the temperature 35.0°. The initial absorbance at 5100 Å was 1.325, and the absorbance values due to  $\text{Fe}(\text{phen})_3^{2+}$  were monitored at 5100 Å (molar absorptivity,  $1.11 \times 10^4 M^{-1} \text{cm}^{-1}$ ) at time intervals appropriate to the speed of the reaction.

When chlorine dioxide was the oxidant, a rapid-mixing technique was employed according to the procedure described previously.<sup>2,4</sup>

## Results and Discussion

The kinetic data were analyzed by means of a non-linear least-squares computer program with unit weights for each datum point. The square of the difference between the observed and calculated absorbance values in terms of the appropriate rate law is minimized and the corresponding standard deviations are calculated directly by means of this program.<sup>2,4,6</sup> A set of typical results for the experiment described above is shown in Table I.

**Dissociation of  $\text{Fe}(\text{phen})_3^{2+}$ .** This reaction has been studied extensively,<sup>7-10</sup> and a stepwise mechanism has been postulated.



The rate-determining step for the dissociation of the complex is postulated to be the loss of the first ligand molecule.

For purposes of comparison and internal consistency, the rate of the dissociation reaction was redetermined. The rate was found to be first order in  $\text{Fe}(\text{phen})_3^{2+}$ . The results are in agreement with those reported by others<sup>7-10</sup> and are shown in Table II. Deviation from first-order behavior occurred usually after 65% reaction. The rate constant values reported in Table II confirm the finding of Lee, Kolthoff, and Leussing<sup>7</sup> that the rate of dissociation is nearly independent of the hydrogen ion concentration.

**Dissociation of  $\text{Fe}(\text{phen})_3^{3+}$ .** Previous investigations<sup>7-9</sup> have shown that this reaction is first order with respect to  $\text{Fe}(\text{phen})_3^{3+}$  and that it can be inhibited by an increase in acid concentration or ionic strength. However, the dissociation products have not been identified clearly. In this investigation, the wavelength of maximum absorption of  $\text{Fe}(\text{phen})_3^{3+}$  was found to be 5900 Å, but no attempt was made to determine the molar absorptivity. Ford-Smith and Sutin<sup>11</sup> report a molar absorptivity of  $870 M^{-1} \text{cm}^{-1}$  at 6020 Å in concentrated sulfuric acid while Murmann and Healy<sup>12</sup>

(7) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *ibid.*, 70, 2348, 3596 (1948).

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(6) H. Fukutomi and G. Gordon, *J. Amer. Chem. Soc.*, 89, 1362 (1967).

report a value of  $175 M^{-1} \text{ cm}^{-1}$  at  $6050 \text{ \AA}$  in concentrated acid solutions.

The rate constant for the dissociation of  $\text{Fe(phen)}_3^{3+}$  was determined at  $35$  and  $25^\circ$ ; the results are shown in Table III.

The dissociation products of concentrated solutions of  $\text{Fe(phen)}_3^{3+}$  are brown in color while those of dilute solutions are yellow. The color also appears to vary with acidity. Detailed spectral analyses are difficult to obtain since aquated  $\text{Fe(III)}$  and its various hydrolytic forms also exhibit absorption bands in the  $3000\text{--}4000\text{-\AA}$  region. Nevertheless, a shoulder was observed at  $3550 \text{ \AA}$  in all solutions of the dissociation products. This shoulder is characteristic of these solutions since it does not appear either in the spectra of aquated  $\text{Fe(III)}$  species or in the spectra of freshly prepared  $\text{Fe(phen)}_3^{3+}$  solutions.

This shoulder can be observed in solutions which contain  $\text{Fe(III)}$  ion and 1,10-phenanthroline in a 1:3 molar ratio. The color of such solutions varies from brown to yellow as the concentration decreases, which is consistent with the dimeric<sup>13</sup> species  $[(\text{phen})_2\text{Fe-O-Fe(phen)}_2]^{4+}$  or  $[(\text{phen})_2\text{Fe(OH)}_2\text{Fe(phen)}_2]^{4+}$ . We did not observe an absorption band at  $5900 \text{ \AA}$  even in solutions of high acidity where  $\text{Fe(phen)}_3^{3+}$  is known to be stable.<sup>13-15</sup>

In many cases the blue solutions of  $\text{Fe(phen)}_3^{3+}$  were observed to revert partially to red.<sup>12</sup> The spectra of the red solutions are identical with those of  $\text{Fe(phen)}_3^{2+}$ . The spectra also exhibit the characteristic absorption shoulder of the iron(III)-phenanthroline dimer at  $3550 \text{ \AA}$ .

Another interesting observation was the very rapid reaction of  $\text{Fe(phen)}_3^{3+}$  with various buffer solutions. The addition of  $\text{Fe(phen)}_3^{3+}$  solution to either acetate, phosphate, or borate buffer mixtures causes a very rapid disappearance of the blue color of  $\text{Fe(phen)}_3^{3+}$ . The reaction of  $\text{Fe(phen)}_3^{3+}$  with sodium hydroxide solutions is also very rapid. Although only preliminary experiments were performed, it seems that  $\text{Fe(phen)}_3^{3+}$  oxidizes either water or hydroxide ions to produce  $\text{Fe(phen)}_3^{2+}$  and probably hydroxyl radicals.<sup>16</sup> It is noteworthy that sulfuric and nitric acids do not react with  $\text{Fe(phen)}_3^{3+}$  while the weak acids do.

**The Reaction between  $\text{Fe(phen)}_3^{2+}$  and Chlorate Ion.** No detectable reaction was found between  $\text{Fe(phen)}_3^{2+}$  and chlorate ion under a variety of conditions. At  $35^\circ$  and an ionic strength of  $1.0 M$  the absorbance due to  $\text{Fe(phen)}_3^{2+}$  remained unchanged after at least 3 hr in mixtures which contained  $2 \times 10^{-3}$  to  $5 \times 10^{-1} M$   $\text{ClO}_3^-$ ,  $2.6 \times 10^{-5}$  to  $1.2 \times 10^{-4} M$   $\text{Fe(phen)}_3^{2+}$ , and  $5 \times 10^{-6}$  to  $5 \times 10^{-4} M$   $\text{H}_2\text{SO}_4$ . In the sulfuric acid concentration range of  $0.05\text{--}0.5 M$  no interaction was detected between  $\text{Fe(phen)}_3^{2+}$  and chlorate ion; the dissociation of  $\text{Fe(phen)}_3^{2+}$  is the only reaction that takes place in this acidity range. This conclusion is confirmed by comparing the dissociation rate constant,  $7.50 \times 10^{-5} \text{ sec}^{-1}$  at  $25^\circ$ , with the observed first-order rate constant,  $7.30 \times 10^{-5} \text{ sec}^{-1}$  at  $25^\circ$ , for the dis-

**Table IV.** The Reaction between Chlorate and Various Metal Ions<sup>a</sup>

Metal ion	$k, M^{-1} \text{ sec}^{-1}$	Ref
U(IV)	$<10^{-6}$	17
V(II)	18.2	18
V(III)	2.0	19
V(IV)	$5.7 \times 10^{-2}$	20
Cr(II)	39.0	2
Fe(II)	$2 \times 10^{-2}$ <sup>b</sup>	21, 22
$\text{Fe(phen)}_3^{2+}$	$<10^{-5}$	This work

<sup>a</sup> Ionic strength  $2.0\text{--}3.0 M$ ,  $0.5\text{--}0.6 M$   $\text{H}^+$ ,  $20^\circ$ . <sup>b</sup> Third-order rate constant for the rate law  $-d[\text{ClO}_3^-]/dt = k[\text{ClO}_3^-][\text{Fe}^{2+}][\text{H}^+]$ , at  $24^\circ$  in the  $0.11\text{--}1.00 M$   $\text{H}^+$  range ( $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  media).

appearance of  $\text{Fe(phen)}_3^{2+}$  in the chlorate-sulfuric acid mixture. Furthermore, the spectra of the products are identical in the acid dissociation reaction and in the reaction where chlorate ion is present.

Of all the chlorine oxidants, chlorate ion is the slowest to react with a variety of metal ions. Furthermore, the rate of reaction in some cases is enhanced by hydrogen ion. Table IV<sup>17-22</sup> lists the rates of chlorate ion reaction with some metal ions.

In neutral or slightly acidic solutions, chlorate ion reactions are extremely slow. As the hydrogen ion concentration is increased to about  $0.1 M$ , the reactivity of chlorate ion is known to increase.<sup>2,22</sup> Under these conditions, chlorate ion oxidizes  $\text{Fe}^{2+}$  slowly, but not  $\text{Fe(phen)}_3^{2+}$  or  $\text{Fe(phen)}_2^{2+}$ . Thus, it appears that complexation of iron(II) with 1,10-phenanthroline inhibits the rate of electron transfer to chlorate ion.

**The Reaction between  $\text{Fe(phen)}_3^{2+}$  and Chlorite Ion.** The study of the reaction between  $\text{Fe(phen)}_3^{2+}$  and chlorite ion in an acetate buffer was initiated by Miyatake.<sup>23</sup> With  $(0.2\text{--}4) \times 10^{-3} M$   $\text{ClO}_2^-$  and  $4 \times 10^{-5} M$   $\text{Fe(phen)}_3^{2+}$  in the pH range  $3.5\text{--}4.5$ , at  $35^\circ$ , a first-order rate constant of  $3.6 \pm 0.2 \times 10^{-4} \text{ sec}^{-1}$  was observed.

It was of continued interest to determine whether the reactions of the chlorine oxidants with  $\text{Fe(phen)}_3^{2+}$  proceed primarily by a one- or a multi-electron process. In a one-electron, outer-sphere oxidation process,  $\text{Fe(phen)}_3^{3+}$  would be the product, but its presence would never be detected owing to the fact that  $\text{Fe(phen)}_3^{3+}$  reacts very rapidly with the buffer constituents. Detection of  $\text{Fe(phen)}_3^{3+}$  is possible when the hydrogen ion concentration is at least  $0.3 M$ , but the  $\text{Fe(phen)}_3^{2+}\text{--ClO}_2^-$  reaction cannot be studied conveniently in this acidity range. Two major problems obtain: the disproportionation of chlorous acid to yield chlorine dioxide which reacts rapidly with  $\text{Fe(phen)}_3^{2+}$ , and the dissociation of  $\text{Fe(phen)}_3^{2+}$ . Thus, for this study, neutral or slightly acidic conditions were chosen for studying the  $\text{Fe(phen)}_3^{2+}\text{--ClO}_2^-$  reaction.

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(21) R. C. Thompson, University of Missouri, unpublished results, 1963.

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(23) R. Y. Miyatake, University of Maryland, unpublished results, 1965.

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

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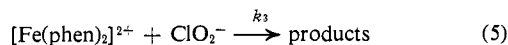
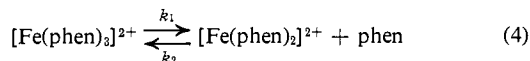
(15) A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, **5**, 1858 (1966).

(16) N. Sutin, quoted in ref 15.

When the concentration of  $\text{ClO}_2^-$  is 10- to 30-fold greater than that of  $\text{Fe}(\text{phen})_3^{2+}$ , the reaction is pseudo first order in  $\text{Fe}(\text{phen})_3^{2+}$ . The same kinetic behavior was observed in neutral unbuffered solutions and in solutions which contained  $5 \times 10^{-6}$  to  $5 \times 10^{-4}$  *M* sulfuric acid. Deviation from first-order behavior occurred usually after 60% reaction. At 35° and an ionic strength of 1.00 *M*, the observed first-order rate constant is  $3.74 \pm 0.05 \times 10^{-4} \text{ sec}^{-1}$  when the concentration of sodium chlorite and  $\text{Fe}(\text{phen})_3^{2+}$  varies from  $2 \times 10^{-3}$  to  $6 \times 10^{-3}$  *M* and  $1.3 \times 10^{-5}$  to  $1.2 \times 10^{-4}$  *M*, respectively.

When the molar chlorite ion concentration is only slightly larger than that of  $\text{Fe}(\text{phen})_3^{2+}$ , marked deviation from first-order behavior takes place after 30% reaction. Addition of more chlorite ion at this stage reinitiates the rapid reaction. This is taken as an indication that part of the original amount of chlorite ion is consumed by another reducing agent. At 35° and an ionic strength of 1.0 *M*, maintained with  $\text{Na}_2\text{SO}_4$ , the average pseudo-first-order rate constant is  $3.74 \times 10^{-4} \text{ sec}^{-1}$ ; when  $4.6 \times 10^{-4}$  *M* free 1,10-phenanthroline is added, the rate constant is  $2.52 \times 10^{-4} \text{ sec}^{-1}$ . In 1.0 *M*  $\text{NaNO}_3$  solution, the average pseudo-first-order rate constant is  $4.58 \times 10^{-4} \text{ sec}^{-1}$ . These effects are similar to those observed for the  $\text{Fe}(\text{phen})_3^{2+}$ - $\text{P}_2\text{O}_8^{4-}$  reaction.<sup>15</sup> Sulfate ion (or  $\text{HSO}_4^-$ ) retards the rate of dissociation more than nitrate ions.<sup>8,9</sup> This is reasonable in that ion-pair formation should be more pronounced in solutions which contain  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{SO}_4^{2-}$  ions than in those which contain  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{NO}_3^-$  ions.

The following mechanism is proposed to account for the observations reported here.



By treating  $\text{Fe}(\text{phen})_2^{2+}$  as an intermediate and assuming that the rate of dissociation of  $\text{Fe}(\text{phen})_3^{2+}$  is slower than the reactions designated by the constants  $k_2$  and  $k_3$ , the following rate law can be derived<sup>15</sup>

$$-\frac{d[\text{Fe}(\text{phen})_3^{2+}]}{dt} = \frac{k_1 k_3 [\text{Fe}(\text{phen})_3^{2+}] [\text{ClO}_2^-]}{k_2 [\text{phen}] + k_3 [\text{ClO}_2^-]} \quad (6)$$

which can be rewritten as

$$-\frac{d[\text{Fe}(\text{phen})_3]^{2+}}{dt} = k_{\text{obsd}} [\text{Fe}(\text{phen})_3]^{2+} \quad (7)$$

At high chlorite ion concentration and low phenanthroline concentration, the observed first-order rate constant,  $k_{\text{obsd}}$ , should approach  $k_1$ . The first-order rate constants reported here are in excellent agreement with the first-order dissociation rate constants<sup>7-10</sup> of  $\text{Fe}(\text{phen})_3^{2+}$ .

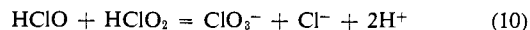
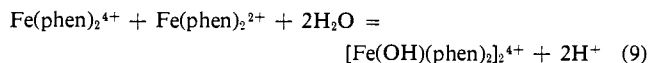
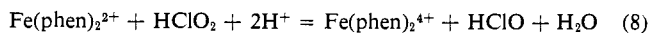
In view of the fact that the  $\text{Fe}(\text{phen})_3^{2+}$ - $\text{ClO}_2^-$  reaction proceeds by dissociation of  $\text{Fe}(\text{phen})_3^{2+}$ , it is concluded that  $\text{Fe}(\text{phen})_3^{3+}$  cannot be the product. The reaction of  $\text{ClO}_2^-$  with  $\text{Fe}(\text{phen})_2^{2+}$  (eq 5) may proceed *via* an outer- or inner-sphere path. In an outer-sphere mechanism, the rate of exchange of the water molecules in the first coordination sphere of  $\text{Fe}(\text{phen})_2^{2+}$  with solvent may be slower than the rate of oxidation. In order to distinguish between an outer-

or inner-sphere path, the rate of aquation and the value of  $k_3$  must be known. Unfortunately, the rate of aquation has not been measured. The value of  $k_3$  can be estimated, however, provided  $k_2$  is known and by considering the variation of the rate of reaction with added phenanthroline. The value of  $k_2$  is known<sup>24</sup> to be  $2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ . By equating eq 6 and 7 and by making the appropriate substitutions, the value of  $k_3$  can be calculated to be  $\approx 3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ . It is noteworthy that the rate constant for the  $\text{Fe}(\text{phen})_2^{2+}$ - $\text{P}_2\text{O}_8^{4-}$  reaction has been estimated<sup>15</sup> in a similar fashion to be also  $\approx 3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ .

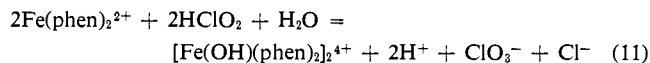
The iron(III)-phenanthroline dimer,  $[(\text{phen})_2\text{Fe}-\text{O}-\text{Fe}(\text{phen})_2]^{4+}$  or  $[(\text{phen})_2\text{Fe}(\text{OH})_2\text{Fe}(\text{phen})_2]^{4+}$ , is a major product of the reaction with chlorite ion. Since the rates of formation and dissociation of this dimer and the dependency, if any, on hydrogen ion concentration are not known, it is difficult to say whether the dimer forms from a reaction of hydrolytic forms of iron(III) with phenanthroline or whether it forms from a reaction of  $\text{Fe}(\text{IV})$  species with  $\text{Fe}(\text{phen})_2^{2+}$ .

Prediction of the mechanism beyond eq 4 requires more information. Although such information is not available, it is interesting to correlate the results obtained in this work with other observations.

If a two-electron process is involved, then

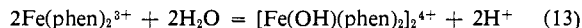
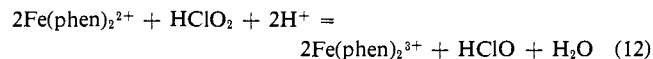


and the net reaction would be



It is known<sup>25</sup> that reaction 10 is fast, and it is expected that reaction 9 would be fast;<sup>26</sup> thus it appears that reaction 8 should be the rate-determining step for this series of reactions. Reaction 8 is faster than the disproportionation<sup>5</sup> of  $\text{HClO}_2$  and the reaction between  $\text{Fe}(\text{phen})_2^{2+}$  and chlorate ion. Such a scheme accounts for formation of  $[\text{Fe}(\text{OH})(\text{phen})_2]_2^{4+}$  and also for the observation that chlorite ion is consumed by a reducing agent other than  $\text{Fe}(\text{phen})_3^{2+}$ .

If a one-electron process is involved, then



would be followed by reaction 10 such that the net process would be given by eq 11. Such a scheme would also account for all the observations. It is relevant to point out that an appreciable amount of chlorate ion is produced in the  $\text{Fe}^{2+}$ - $\text{ClO}_2^-$  reaction<sup>21</sup> where the chlorate ion is postulated<sup>25</sup> to form *via* the interaction of  $\text{HClO}_2$  and  $\text{HOCl}$ .

**The Reaction between  $\text{Fe}(\text{phen})_3^{2+}$  and Chlorine Dioxide.** The reaction between  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{ClO}_2$

(24) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

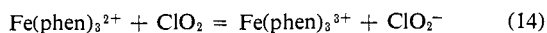
(25) F. Emmenegger and G. Gordon, *ibid.*, **6**, 633 (1967).

(26) By analogy with the  $\text{Fe}^{IV} + \text{Fe}^{II} \rightleftharpoons \text{Fe}^{III}_2$  reaction which is postulated to be fast: T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

was found to yield  $\text{Fe(phen)}_3^{3+}$  as the major iron product when  $\text{ClO}_2$  is in excess and the acid concentration is greater than 1.0 *M*. Under these conditions, the reaction is very rapid and is essentially complete upon mixing. The products are green in color as a result of the presence of excess of  $\text{ClO}_2$  which is yellow and  $\text{Fe(phen)}_3^{3+}$  which is blue.

When the acidity is lower than 0.3 *M* and a slight excess of  $\text{ClO}_2$  is used, the reaction kinetics can be followed by the technique used in this investigation. Formation of the iron(III)-phenanthroline dimer, if any, cannot be detected spectrophotometrically because of the large absorption band due to  $\text{ClO}_2$  around 3600 Å. The reaction is first order in each reactant (concentration range  $1.7 \times 10^{-4}$  to  $6 \times 10^{-4}$  *M*) and independent of the hydrogen ion concentration (0.02–0.3 *M*).

The rate-determining step for the electron transfer from  $\text{Fe(phen)}_3^{2+}$  to chlorine dioxide may be represented as



The second-order rate constant is  $1.86 \pm 0.13 \text{ M}^{-1} \text{ sec}^{-1}$  at 35°. Since the rate of reaction between  $\text{Fe(phen)}_3^{2+}$  and chlorine dioxide is faster than the rate of  $\text{Fe(phen)}_3^{2+}$  dissociation, it is concluded that electron transfer takes place *via* an outer-sphere path.

It should be noted that most reactions between  $\text{Fe(phen)}_3^{2+}$  and many oxidants can be classified into one of two groups based on whether or not  $\text{Fe(phen)}_3^{3+}$  is formed as a product. Thus, reactions of  $\text{Fe(phen)}_3^{2+}$  with  $\text{Ce(IV)}$ ,<sup>27</sup>  $\text{Co(III)}$ ,<sup>27</sup>  $\text{Mn(III)}$ ,<sup>27</sup>  $\text{Cl}_2$ ,<sup>4</sup> and  $\text{ClO}_2$  fall into the first group since they yield  $\text{Fe(phen)}_3^{3+}$  rapidly. Reactions of  $\text{Fe(phen)}_3^{2+}$  with peroxydisphosphate ion<sup>15</sup> and chlorite ion fall into the second group since they are slow and do not yield  $\text{Fe(phen)}_3^{3+}$  as a product.

Reactions of the first group are first order in each reactant and usually take place in acidic solutions. These reactions, which involve one-equivalent oxidizing agents, proceed *via* an outer-sphere path since electron transfer takes place rapidly and the first coordination sphere of the iron complex retains the same ligands throughout the process.

Reactions of the second group take place in the 1.0–9.0 pH range; their rates are controlled by the

(27) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1019 (1964).

first dissociation step,  $\text{Fe(phen)}_3^{2+} \rightleftharpoons \text{Fe(phen)}_2^{2+} + \text{phen}$ , and are usually independent of oxidant concentration. These reactions involve multiequivalent oxidants. Electron transfer from  $\text{Fe(phen)}_2^{2+}$  to the oxidizing agent may take place *via* an outer-sphere path only if the rate of exchange between solvent and the water molecules in the first coordination sphere of  $\text{Fe(phen)}_2^{2+}$  is slower than the rate of oxidation.

Several multiequivalent oxidants such as  $\text{Cr(VI)}$ , peroxydisulfate ion, and lead dioxide react with  $\text{Fe(phen)}_3^{2+}$  rapidly to form  $\text{Fe(phen)}_3^{3+}$ . These reactions belong in the first group, but their mechanism must involve a one-equivalent process. For example,  $\text{Cr(V)}$  has been postulated<sup>28</sup> as an intermediate in the  $\text{Fe(phen)}_3^{2+}$ - $\text{Cr(VI)}$  reaction. Sulfate radical is proposed<sup>29</sup> also as an intermediate in the  $\text{Fe(phen)}_3^{2+}$ -peroxydisulfate ion reaction. Although no kinetic studies have been reported on the  $\text{Fe(phen)}_3^{2+}$ - $\text{PbO}_2$  reaction, formation of  $\text{Pb(III)}$  as an intermediate could be postulated since  $\text{Fe(phen)}_3^{3+}$  is the product.

Preliminary experiments have revealed that the  $\text{Fe(phen)}_3^{2+}$ - $\text{MnO}_2$  reaction yields  $\text{Fe(phen)}_3^{3+}$  as a product. Thus, reduction of  $\text{Mn(IV)}$  to  $\text{Mn(II)}$  involves two one-electron steps in this reaction. Another preliminary experiment revealed that the  $\text{Fe(phen)}_3^{2+}$ - $\text{H}_2\text{O}_2$  reaction belongs in the second group. Formation of  $\text{Fe(phen)}_3^{3+}$  could not be detected even when the oxidant concentration was 100-fold in excess and the acidity was sufficiently high to stabilize  $\text{Fe(phen)}_3^{3+}$  if it were formed. The major product formed was the iron(III)-phenanthroline dimer. Therefore, it is suggested that reduction of  $\text{H}_2\text{O}_2$  by  $\text{Fe(phen)}_3^{2+}$  does not involve an outer-sphere, one-electron process.

In conclusion, it should be noted that coordination of ligands to metal ions can either facilitate or retard the rates of oxidation of these ions. It appears that complexed iron(II) species such as  $\text{Fe(phen)}_3^{2+}$  and  $\text{Fe(CN)}_6^{4-}$  react slower than  $\text{Fe}^{2+}$ .

**Acknowledgments.** The authors wish to express their appreciation to the U. S. Atomic Energy Commission for its financial support through Grant No. At-(40)-2858.

(28) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963).

(29) J. Burgess and R. H. Prince, *J. Chem. Soc.*, **A**, 1772 (1966).