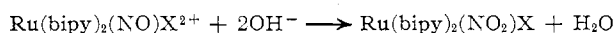


these and other substrates with coordinated nitrosyl is currently under investigation.

Coordinated  $\text{NO}^+$  would also seem to be a likely leaving group in the acid-catalyzed aquation of metal nitrite complexes. However, this has been shown not to be the case in the acid-catalyzed removal of nitrite from  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ .<sup>16</sup>

All of the nitrosyl complexes reported here react rapidly in solution with hydroxide ion to give deep red-brown solutions of the corresponding nitrite complexes.<sup>7</sup> Reconversion to the nearly colorless nitrosyl complexes occurs by making the solutions acidic. We have described in the Experimental Section the preparations of  $[\text{Ru}(\text{bipy})_2(\text{NO}_2)_2] \cdot \text{H}_2\text{O}$  and  $[\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}] \cdot \text{H}_2\text{O}$  by reaction with hydroxide



In addition to the ruthenium chelate complexes reported here both  $\text{Fe}(\text{CN})_5\text{NO}^{2-}$  and  $\text{Ru}(\text{CN})_5\text{NO}^{2-}$  react with hydroxide to give the corresponding nitrite complexes  $\text{Fe}(\text{CN})_5\text{NO}_2^{4-}$ ,<sup>13,17</sup> and  $\text{Ru}(\text{CN})_5\text{NO}_2^{4-}$ .<sup>18</sup> Activation of coordinated nitrosyl to attack by bases

(16) A. D. Harris, R. Stewart, D. Hendrickson, and W. L. Jolly, *Inorg. Chem.*, **6**, 1052 (1967).

(17) J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 385 (1967).

(18) E. J. Barans and A. Müller, *Chem. Ber.*, **102**, 3915 (1969).

seems to occur only when back-bonding ligands in addition to nitrosyl groups are coordinated to the metal. In other complexes, reactions with hydroxide or other bases result in ligand displacement and the metal-nitrosyl linkage is unreactive.<sup>1</sup>

The relatively high infrared stretching frequencies for coordinated NO in these complexes are indicative that a high degree of positive charge resides on the coordinated nitrosyl. Values for  $\nu_{\text{NO}}$  in acetone are from 1930 to 1951  $\text{cm}^{-1}$  for the ruthenium chelate complexes and 1937 and 1930  $\text{cm}^{-1}$  in mulls for  $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$  and  $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]$ , respectively.<sup>10</sup> The high  $\nu_{\text{NO}}$  values, diamagnetism of the complexes, and facile interconversion between coordinated nitrite and coordinated nitrosyl all indicate that the bipyridine and phenanthroline complexes contain essentially ruthenium(II) and bound nitrosyl with a high degree of positive charge.

**Acknowledgments.**—Acknowledgment is made to the University Research Council of the University of North Carolina, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the National Science Foundation for a Science Development Award to our department, Agency No. GU 2059.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY OF IOWA, IOWA CITY, IOWA 52240

## The Reaction of Tris(1,10-phenanthroline)iron(II) Ion with Chlorine(I) Species

By MARTIN G. ONDRUS AND GILBERT GORDON\*

Received August 26, 1970

Hypochlorous acid reacts with  $\text{Fe}(\text{phen})_3^{2+}$  by two paths, one which is dependent upon dissociation of the iron complex and one which is independent of dissociation. The reaction was studied at 15, 25, and 40° under pseudo-first-order conditions with the oxidant being in excess. At 25° and constant pH, plots of the pseudo-first-order rate constant as a function of  $[\text{Cl(I)}]$  are linear with equal nonzero intercepts and slopes that increase with increasing  $[\text{H}^+]$ . The pseudo-first-order rate constant is given by

$$k_{\text{obsd}} = k_0 + \left[ \frac{k_1[\text{H}^+]/K + k_2}{[\text{H}^+]/K + 1} \right] [\text{Cl(I)}]$$

At 25°  $k_0 = (7.5 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$ ,  $k_1 = (2.2 \pm 0.14) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $k_2 = (2.0 \pm 0.16) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ . The rate constants were calculated using a value of  $2.90 \times 10^{-8}$  for the acid dissociation constant of hypochlorous acid at 25°.

### Introduction

Hypochlorous acid reacts much more rapidly than does chlorine in solution with aquated iron(II).<sup>1</sup> However, preliminary work by Shakhashiri and Gordon indicates that oxidation of the tris(1,10-phenanthroline)iron(II) complex by hypochlorous acid is considerably slower than when chlorine is the oxidizing agent.<sup>2</sup>

The reaction of hypochlorous acid with tris(1,10-

phenanthroline)iron(II) ion in acid solution is autocatalytic; as the reaction proceeds, chloride ion formed as a product reacts with hypochlorous acid to produce chlorine appropriate to the equilibrium



Since tris(1,10-phenanthroline)iron(II) ion is stable in the pH region 2–9,<sup>3</sup> we have attempted to eliminate chlorine interference by studying the reaction at high pH where chlorine is absent.

(3) W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

(1) T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).

(2) B. Z. Shakhashiri and G. Gordon, *Inorg. Chem.*, **7**, 2454 (1968).

## Experimental Section

Chlorine(I) solutions were prepared and analyzed by standard methods.<sup>4</sup> Solutions were stable for several weeks when stored in the dark at 0° either as chlorine monoxide dissolved in carbon tetrachloride or as a basic solution of sodium hypochlorite. For reactions in acid solution, where hypochlorous acid was the principal oxidizing species, solutions were prepared from chlorine monoxide and analyzed within several hours of the kinetic run. Spectral analysis at several wavelengths<sup>5</sup> indicated that hypochlorous acid with no added strong acid contained less than 0.5% chlorine.

In most cases, tris(1,10-phenanthroline)iron(II) ion was prepared in solution by adding a stoichiometric quantity of 1,10-phenanthroline monohydrate to standard iron(II) sulfate solutions. A few solutions were prepared directly from the solid tris(1,10-phenanthroline)iron(II) perchlorate salt. The solid was made by precipitating the metal complex, in the presence of excess 1,10-phenanthroline, with dilute perchloric acid.

Ionic strength was maintained at  $1.0 \pm 0.05 M$  with sodium sulfate. Stock sodium sulfate solutions were prepared from Baker Analyzed reagent grade Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O which had been recrystallized twice. In all solutions conductivity water, obtained by passing distilled water through Barnstead organic and inorganic removal columns, was utilized.

Kinetic runs were carried out on a Cary 14R recording spectrophotometer with a cell compartment thermostated to  $\pm 0.05^\circ$ . Temperature in the cell compartment was measured by means of a Dymec quartz thermometer. A Radiometer Model 26 pH meter was used to obtain initial pH values for each run with the temperature being maintained within  $\pm 0.5^\circ$  of the actual kinetic run.

In a given experiment, the reactants were mixed in a constant-temperature bath outside the Cary cell compartment and transferred into a 0.5-cm cell within the spectrophotometer. The progress of the reaction was followed at 510 nm where tris(1,10-phenanthroline)iron(II) has an absorption maximum. Sodium borate buffer (0.01–0.015 M) was present in most runs where the pH was greater than 7. Experiments with no buffer present indicated that initial rates are not affected by the presence of small amounts of borate. Reactions were carried out under pseudo-first-order conditions with 10–200-fold excess chlorine(I), and initial  $k_{\text{obsd}}$  values were obtained from absorbance data for the linear portion of the reaction. Apparent rate constants from replicate runs in buffered solutions differed from the mean by less than 5%.

## Results

At pH values greater than 7, the reaction of Fe(phen)<sub>3</sub><sup>2+</sup> with chlorine(I) in excess shows deviations from first-order behavior which are independent of chloride ion concentration. The pH decreases slowly during the course of the reaction, which appears to account for the observed deviations. Dilute sodium borate buffer in the reaction mixture reduced deviations to the point that initial rates could be measured quite accurately but, in most cases, did not completely eliminate the problem. Consequently, our  $k_{\text{obsd}}$  values represent from 10% to greater than 50% reaction at pH >7 and 2–4% reaction at pH 5.

Measured  $k_{\text{obsd}}$  values at 15, 25, and 40° are given in Table I. At 25° and constant pH, plots of  $k_{\text{obsd}}$  as a function of [Cl(I)] are linear with equal nonzero intercepts and slopes that increase with increasing [H<sup>+</sup>] as

TABLE I

OBSERVED FIRST-ORDER RATE CONSTANTS <sup>a</sup> AT pH 8–9			
10 <sup>2</sup> [Cl(I)], M	pH	10 <sup>4</sup> $k_{\text{obsd}}$ , sec <sup>-1</sup>	10 <sup>4</sup> $k_{\text{calcd}}$ , <sup>b</sup> sec <sup>-1</sup>
25.0°			
0.16	8.08	0.83	0.83
0.42	8.08	1.02	1.01
0.28	8.39	0.89	0.87
0.32	8.42	0.93	0.89
0.47	8.42	0.97	0.96
1.34	8.38	1.34	1.36
1.62	8.37	1.46	1.50
2.58	8.38	2.00	1.94
2.79	8.37	1.96	2.05
0.19	8.85	0.79	0.81
0.61	8.81	0.92	0.94
0.78	8.83	0.97	0.99
1.01	8.82	1.01	1.06
1.16	8.77	1.12	1.11
1.55	8.81	1.20	1.22
1.97	8.85	1.30	1.33
2.22	8.81	1.46	1.42
2.23	8.82	1.43	1.42
2.76	8.81	1.60	1.58
4.22	8.81	2.00	2.01
1.37	9.05	1.17	1.11
40.0°			
0.67	8.69	10.1	10.7
0.78	8.05	11.3	11.5
0.89	8.61	10.7	11.1
0.94	8.59	10.9	11.2
0.95	8.10	13.3	11.9
0.98	8.11	12.2	12.0
1.13	8.38	11.8	11.9
1.20	8.27	12.4	12.2
1.50	8.43	13.1	12.6
1.72	8.38	13.8	13.2
15.0°			
0.87	8.16	0.30	0.32
1.21	8.03	0.45	0.45
1.89	8.87	0.29	0.29
2.11	9.05	0.29	0.28
2.26	8.42	0.49	0.47
2.36	8.50	0.49	0.45
2.61	8.74	0.34	0.39
3.20	8.64	0.54	0.49

<sup>a</sup> [Fe(phen)<sub>3</sub><sup>2+</sup>]<sub>0</sub> varied from 0.8 to  $1.8 \times 10^{-4} M$ , and [Cl<sup>-</sup>] varied from  $10^{-5}$  to 0.5 M. <sup>b</sup> Calculated by a subroutine of our nonlinear least-squares program.  $K = 2.90 \times 10^{-8}$  at 25°,  $2.33 \times 10^{-8}$  at 15°, and  $3.78 \times 10^{-8}$  at 40°. The values of  $K$  at 15 and 25° were taken directly from ref 7 and at 40° by extrapolation from the data at lower temperatures.

shown in Figure 1. The data are consistent with the following pseudo-first-order rate constant

$$k_{\text{obsd}} = k_0 + \left[ \frac{k_1[\text{H}^+]/K + k_2}{[\text{H}^+]/K + 1} \right] [\text{Cl(I)}] \quad (2)$$

At 25°,  $k_0 = (7.5 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$ ,  $k_1 = (2.2 \pm 0.14) \times 10^{-2} M^{-1} \text{ sec}^{-1}$ , and  $k_2 = (2.0 \pm 0.16) \times 10^{-3} M^{-1} \text{ sec}^{-1}$ . The individual rate constants were calculated from  $k_{\text{obsd}}$  as a function of hydrogen ion and hypochlorous acid concentrations by means of a nonlinear least-squares program<sup>6</sup> using a value of  $2.90 \times$

(4) G. H. Cady, *Inorg. Syn.*, **5**, 160 (1957).

(5) G. Zimmerman and F. C. Strong, *J. Amer. Chem. Soc.*, **79**, 2063 (1957).

(6)  $k_{\text{obsd}}$  data at each temperature were analyzed with unit weights for each datum point in terms of the rate constant given by eq 2. The computer program minimizes the square of the differences between the observed and calculated  $k_{\text{obsd}}$  values.

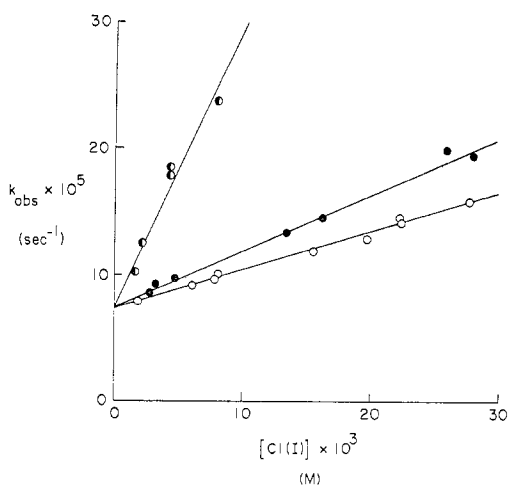


Figure 1.—Plot of the apparent rate constant as a function of chlorine(I) concentration at unit ionic strength and 25°: ○, pH 8.82 ± 0.03; ●, pH 8.40 ± 0.03; ●, pH 5.0 ± 0.2.

$10^{-8}$  for the acid dissociation constant<sup>7</sup> of hypochlorous acid. The uncertainties correspond to computer-calculated standard deviations.

The  $k_0$  pathway is apparently dependent upon the rate of dissociation of the  $\text{Fe}(\text{phen})_3^{2+}$  complex. This was further substantiated by observing inhibition of the reaction resulting from the presence of excess phenanthroline ligand. The rate of dissociation of  $\text{Fe}(\text{phen})_3^{2+}$  was measured also at 15 and 40° in 0.50 M  $\text{H}_2\text{SO}_4$  such that a direct comparison would be possible. The first-order rate constants, listed in Table II, for dissociation

TABLE II  
DISSOCIATION RATE CONSTANT OF  
 $\text{Fe}(\text{phen})_3^{2+}$  IN SULFURIC ACID

$10^5 k_d$ , sec <sup>-1</sup>	Temp, °C	Ref	$10^5 k_d$ , sec <sup>-1</sup>	Temp, °C	Ref
1.2	15.0	a	38	35.0	c
7.5	25.0	b	90	40.0	a

<sup>a</sup> This paper. <sup>b</sup> T. S. Lee, I. M. Kolthoff, and D. L. Luessing, *J. Amer. Chem. Soc.*, **70**, 2348, 3596 (1948). <sup>c</sup> J. Burgess and R. H. Prince, *J. Chem. Soc.*, 6061 (1965).

of the complex are in reasonable agreement with the values of  $k_0$  found at these temperatures.<sup>8</sup>

Although the reaction is autocatalytic in acid solution, some runs were carried out at a pH of approximately 5 to test the validity of the rate law. In these experiments, the hydrogen ion concentration was determined entirely by dissociation of HOCl since no additional acid or base had been added. Under these conditions, the rate law simplifies to a form independent of  $[\text{H}^+]$

$$k_{\text{obsd}} = k_0 + k_1[\text{Cl(I)}] \quad (3)$$

The average value for  $k_1$  of  $(2.2 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  calculated from the data listed in Table III is in good agreement with  $k_1$  observed at lower hydrogen ion concentrations.

Since two distinct reaction pathways are apparent,

(7) J. C. Morris, *J. Phys. Chem.*, **70**, 3798 (1966).

(8) At 15.0°,  $k_0 = (7.8 \pm 4.6) \times 10^{-6} \text{ sec}^{-1}$ , and at 40.0°,  $k_0 = (8.3 \pm 0.5) \times 10^{-4} \text{ sec}^{-1}$ .

TABLE III  
INITIAL OBSERVED RATE CONSTANTS AT pH 5 AND 25°

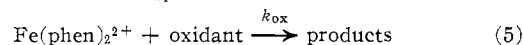
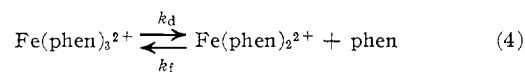
$10^5 k_{\text{obsd}}$ , sec <sup>-1</sup>	$10^3 [\text{HOCl}]$ , M	$10^2 k_1$ , <sup>a</sup> M <sup>-1</sup> sec <sup>-1</sup>	$10^5 k_{\text{obsd}}$ , sec <sup>-1</sup>	$10^3 [\text{HOCl}]$ , M	$10^2 k_1$ , <sup>a</sup> M <sup>-1</sup> sec <sup>-1</sup>
17.9	4.31	2.41	12.5	2.16	2.31
23.8	7.97	2.05	10.3	1.50	1.87
18.5	4.31	2.55			

<sup>a</sup> Determined by assuming  $k_0 = 7.5 \times 10^{-5} \text{ sec}^{-1}$ .

one which is dependent upon dissociation of the complex and the other which is independent of dissociation, we expected to see a mixture of iron(III) products.  $\text{Fe}(\text{phen})_3^{3+}$  reacts readily with buffers such as sodium borate, so its formation would not be observed when borate is present. However, repetitive spectral scans of the reaction at pH 5 with no borate present showed no change in absorbance at 600 nm where  $\text{Fe}(\text{phen})_3^{3+}$  has an absorption maximum. Furthermore, the decrease in absorbance at 510 nm was accompanied by the appearance of a shoulder at 360 nm, characteristic of the dimeric iron(III)-phenanthroline complex,<sup>9</sup> and an isosbestic point at 390 nm. This indicates that if  $\text{Fe}(\text{phen})_3^{3+}$  is an intermediate product, it reacts so rapidly to form the hydrolytic dimer,  $[\text{Fe}(\text{phen})_2\text{OH}]_2^{4+}$  or  $\text{Fe}(\text{phen})_2\text{OFe}(\text{phen})_2^{4+}$ , that its presence cannot be observed.

### Discussion

A number of redox reactions which involve  $\text{Fe}(\text{phen})_3^{2+}$  as the reductant are known to proceed *via* one-electron, outer-sphere mechanisms with pale blue  $\text{Fe}(\text{phen})_3^{3+}$  being the iron(III) product. However, in a few cases, notably the reactions of the iron(II) complex with peroxydiphosphate ion,<sup>10</sup> chlorite ion,<sup>11</sup> and hydrogen peroxide,<sup>12</sup> a different mechanism is observed. The rate of reaction with these multiequivalent oxidants is determined by the rate of dissociation of the iron(II) complex, and the only iron product is the iron(III)-phenanthroline dimer. The proposed mechanism is



The steady-state approximation ( $k_d \ll k_f$  and  $k_{\text{ox}}$ ) gives rise to the rate law

$$-\frac{d[\text{Fe}(\text{phen})_3^{2+}]}{dt} = \frac{k_{\text{ox}} k_d [\text{Fe}(\text{phen})_3^{2+}] [\text{oxidant}]}{k_f [\text{phen}] + k_{\text{ox}} [\text{oxidant}]} \quad (6)$$

Under conditions where the oxidant is in excess and little free phenanthroline is present, the rate law takes on the simplified form

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

(9) A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, **74**, 4744 (1952).

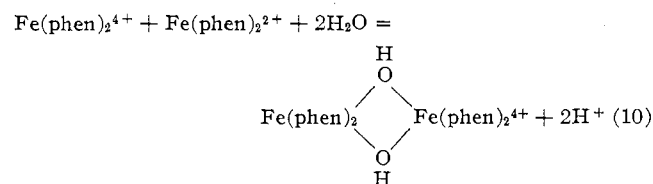
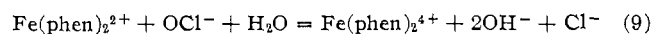
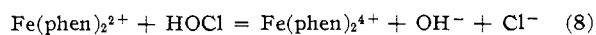
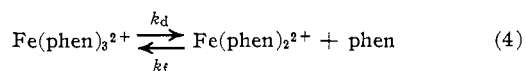
(10) A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, **5**, 1858 (1966). These workers observed an isosbestic point at 375 nm and the appearance of peaks at 345 and 360 nm in the reaction of tris(1,10-phenanthroline)iron(II) ion with peroxydiphosphate. Evidence cited by them for some ligand oxidation by peroxydiphosphate may account for the difference between their observed product spectra and our own.

(11) B. Z. Shakhshiri and G. Gordon, *J. Amer. Chem. Soc.*, **91**, 1103 (1969).

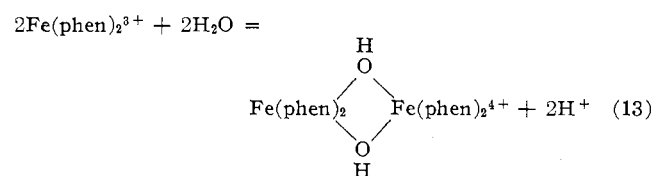
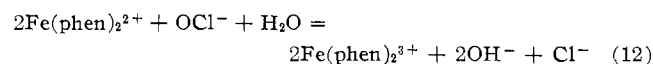
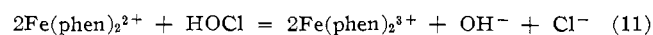
(12) J. Burgess and R. H. Prince, *J. Chem. Soc.*, 6061 (1965).

Under certain conditions, hypochlorous acid and hypochlorite ion fall into this category. The conclusion that the  $k_0$  term arises from Fe(phen)<sub>3</sub><sup>2+</sup> dissociation is apparent from measured values of  $k_d$ , the observation that excess phenanthroline inhibits the reaction rate, and the fact that this term is zero order in total chlorine(I) concentration.

Mechanistically, this pathway may involve a two-electron oxidation of Fe(phen)<sub>2</sub><sup>2+</sup> where reactions 8-10 are very fast. However, a one-electron mechanism



cannot be ruled out. According to such a scheme reactions 11-13 would follow the rate-determining dissociation step.



Activation parameters for  $k_0$ ,  $k_1$ , and  $k_2$  were calculated simultaneously using a subroutine of our non-linear least-squares program.<sup>13</sup> The values are listed in Table IV where the uncertainties represent the

TABLE IV  
ACTIVATION PARAMETER DATA FOR THE  
Fe(phen)<sub>3</sub><sup>2+</sup>-Cl(I) REACTION<sup>a</sup>

Rate constant	$\Delta H^*$ , kcal/mol	$\Delta S^*$ , eu	Rate constant	$\Delta H^*$ , kcal/mol	$\Delta S^*$ , eu
$k_d$	$30.2 \pm 0.3$	$23.7 \pm 1.1$	$k_1$	$16.2 \pm 2$	$-11.6 \pm 6$
$k_0$	$30.5 \pm 0.6$	$24.8 \pm 1.9$	$k_2$	$25.3 \pm 2.8$	$14.1 \pm 9.5$

<sup>a</sup> Activation parameters associated with  $k_1$  should be taken only as lower limits since they are based upon relatively small changes in hydrogen ion concentration.

computer-calculated standard deviations. Fitted  $k_{\text{obsd}}$  values obtained in this manner are listed in column 4 of Table I. The activation parameters for  $k_0$  agree to better than one standard deviation with  $\Delta H^*$  and  $\Delta S^*$  measured for  $k_d$ . The values of  $\Delta H^*$  and  $\Delta S^*$  for com-

(13) Activation parameters for  $k_0$ ,  $k_1$ , and  $k_2$  were calculated simultaneously in terms of eq 2.  $k_{\text{obsd}}$  was input as the dependent variable, and temperature, [Cl(I)], and [H<sup>+</sup>] were independent variables. Data points were weighted according to the square of the reciprocal of the dependent variable such that the per cent deviation was minimized.

plex dissociation were calculated using data from Table II.

The rate constants  $k_1$  and  $k_2$  belong to a dissociation-independent oxidation of Fe(phen)<sub>3</sub><sup>2+</sup> by hypochlorous acid and hypochlorite ion, respectively. The mechanism probably involves a one-electron oxidation similar to the oxidation of Fe(phen)<sub>3</sub><sup>2+</sup> by chlorine or chlorine dioxide. Such a mechanism is expected to yield Fe(phen)<sub>3</sub><sup>3+</sup> as a product. However, Fe(phen)<sub>3</sub><sup>3+</sup> is unstable in solutions containing low hydrogen ion concentration and decomposes readily to the yellow dimer. The magnitudes of the enthalpies of activation assigned to these rate constants are not unreasonable. They reflect the two-electron oxidant chlorine(I) reacting by a less favorable one-electron pathway. An outer-sphere or nonbridging two-electron transfer reaction seems less likely. The Franck-Condon barrier for such a mechanism would be exceptionally high.<sup>14</sup>

Several known two-electron oxidizing agents react with Fe(phen)<sub>3</sub><sup>2+</sup> by a one-electron mechanism with Fe(phen)<sub>3</sub><sup>3+</sup> being the product. Peroxydisulfate ion<sup>15,16</sup> is one such species and is known to react following a preliminary ion-pair formation. At 25° the forward rate constant for oxidation of Fe(phen)<sub>3</sub><sup>2+</sup> is 0.210 M<sup>-1</sup> sec<sup>-1</sup>. A recent study by Burgess indicated that thallium(III) also reacts with Fe(phen)<sub>3</sub><sup>2+</sup> by a slow dissociation-independent path. Unfortunately, a second-order rate constant for that reaction has not yet been determined due to the significant decrease in activity of thallium(III) with time.<sup>17</sup>

One conclusion which is apparent from this and related studies is that two-electron transfer does not occur unless the first coordination sphere of the reducing agent is penetrated by the oxidizing agent. It should also be noted that although this appears to be a necessary condition, it is not a sufficient condition in that many reactions which occur by an inner-sphere pathway are not two-electron reactions. Our studies on systems which involve halogen oxidants indicate that two-electron-transfer reactions also appear to be associated with oxygen bonding in the first coordination sphere.<sup>18,19</sup> The lack of two-electron transfer or the preference for one-electron transfer in systems which occur by means of inner-sphere or pseudo-inner-sphere (seven-coordinated intermediates) pathways may be associated with direct halogen bonding—rather than oxygen bonding. One last point worth noting is that we have not discovered any examples of direct two-electron-transfer reactions which can be classified as truly outer-sphere reactions.

**Acknowledgments.**—The authors wish to express their appreciation to the Atomic Energy Commission for financial support under Contract AT(11-1)-1780 and to NASA for a traineeship.

- (14) J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 18 (1960).  
 (15) J. Burgess and R. H. Prince, *J. Chem. Soc. A*, 1772 (1966).  
 (16) S. Raman and C. H. Brubaker, Jr., *J. Inorg. Nucl. Chem.*, **31**, 1091 (1960).  
 (17) J. Burgess, *J. Chem. Soc. A*, 3123 (1968).  
 (18) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).  
 (19) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).