

ABSTRACT

The rate constant for the $\text{Tl(III)}-\text{Fe(phen)}_3^{2+}$ reaction has been measured for thallium(III) concentrations greater than $4.74 \times 10^{-3} \text{ M}$ at $\mu = 3.0$. The value for the rate constant at 25°C . is $4.79 \times 10^{-2} \text{ liter mole}^{-1}\text{sec}^{-1}$; at 30°C . the rate constant is approximately $0.528 \text{ liter mole}^{-1}\text{sec}^{-1}$. The reaction appears to be second order.

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = k [\text{Fe(phen)}_3^{2+}] (\text{Tl}^{3+})$$

At thallium(III) concentrations less than $4.74 \times 10^{-3} \text{ M}$ the iron phenanthroline complex dissociates rapidly, and the oxidation reaction occurs simultaneously. When lanthanum(III) was substituted for thallium(III), it was noted that

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

The rate constants were calculated; k_1 is $8.87 \times 10^{-2} \text{ mole liter}^{-1}\text{sec}^{-1}$ and k_2 is $5.95 \times 10^{-2} \text{ sec}^{-1}$.

A KINETIC STUDY OF THE
THALLIUM(III)-TRIS-(1,10-PHENANTHROLINE)IRON(II) ION
REACTION IN NITRIC ACID SOLUTIONS

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DEDICATION

To Mom and Dad

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INTRODUCTION

A study of the Thallium(III)-Tris-(1,10-phenanthroline) iron(II) system at high thallium(III) concentration indicated that an oxidation reaction which was first order in each of the reactants occurred in perchlorate solutions. It appeared that a similar result should be obtained using lower thallium concentrations.

If the nitrate radical did not cause a specific anion effect, a result analogous to that obtained for the perchlorates should be discovered in nitrate solutions. A series of experiments with varied thallium(III), iron-phenanthroline complex and hydrogen ion concentrations was performed to determine the course of the reaction and its rate in nitrate solutions.

HISTORICAL

The first studies on the iron-phenanthroline system performed in 1936 showed that the intense absorption bands of the complex in the visible region were readily distinguishable from the ligand bands appearing at approximately 270 $m\mu$, which were not due to the electronic transitions of the specific cation.(1)

Kolthoff, Lee and Leussing(2) conducted equilibrium studies on tris-(1,10-phenanthroline)iron(II) complexes and determined that the equilibrium constant, K' , was 5×10^{-22} for the reaction,



For the dissociation in acid solution the equilibrium constant, K'' , was 4×10^{-7} for the reaction,



The calculated rate constant for the dissociation reaction in 1 M acid was $7.5 \times 10^{-5} \text{ sec}^{-1}$.(2,3) The half-life in acid solution was approximately 2.5 hours at 25°C.

In acid solution phenanthroline adds only one proton due to steric factors. The mono- and the bis- as well as the tris-(1,10-phenanthroline)iron(II) ions are present in appreciable concentrations. In neutral solutions only the tris-(1,10-phenanthroline)iron(II) concentration is appreciable.(4)

Basolo, Hayes and Neumann(3) determined the dissociation constants for tris-(1,10-phenanthroline)iron(II) ion in nitric acid. Their results are as follows:

| Temperature (°C) | k_{diss} (sec ⁻¹) |
|------------------|--|
| 25.3 | 7.38×10^{-5} |
| 30.9 | 1.97×10^{-4} |
| 34.6 | 3.70×10^{-4} |

Increasing the concentration of nitric acid from 0.01 M to 1.79 M causes a decrease in k_{diss} from 7.57×10^{-5} sec⁻¹ to 6.13×10^{-5} sec⁻¹. When potassium nitrate is added, the rate constant increases with increasing potassium nitrate concentration. The addition of increasing amounts of lithium nitrate caused a decrease in the rate constants.(5)

The first kinetic studies of the Tl(I)-Tl(III) exchange reaction were conducted by Prestwood and Wahl(6) by using radioactive Tl(III). Perchloric acid solutions with sodium nitrate added to regulate the ionic strength were used. The rate of the reaction varied with the acid concentration and with the acid used. The rate was greater in nitric and hydrochloric acids than in perchloric acid. The maximum rate in each acid was observed at 1 M acid concentration. The addition of lithium perchlorate to perchlorate solutions increased the rate of exchange.

The Tl(I)-Tl(III) system was first order in total concentration of thallium(I) and first order in thallium(III).

The rate of exchange decreased with an increase in hydrogen ion concentration. Both $Tl(III)$ and $TlOH^{2+}$ were considered present in significant concentrations, but only $TlOH^{2+}$ was assumed to exchange with $Tl(I)$.(7)

In the $Fe(II)$ - $Tl(III)$ system the rate constant decreased when the hydrogen ion concentration was increased from 0.75 M to 1.5 M. When the hydrogen ion concentration was increased from 2 M to 4 M, the rate constant increased. The rate constant decreased slightly after the reaction was 50-70% complete. In the absence of oxygen this decrease was not noted.(8)

Johnson(9) studied the same system. Hydrogen ion concentrations large enough to be considered constant throughout each run were used. The rate constant was identical for excess iron and excess thallium. Hydrolysis products of thallium were assumed to be important in the rate determining step.

The pH dependence of the electron exchange between $Tl(I)$ and $Tl(III)$ in perchloric acid solutions was studied by Born, Vogg and Vogt(10), who postulated that an increase in hydrogen ion yielded complex formation between $Tl(III)$ and perchlorate radicals. The rate constant equalled $3.33 \times 10^{-5} \text{ sec}^{-1}$.

Dulz and Sutin investigated the kinetics of the tris-(1,10-phenanthroline)iron(II)- $Ce(IV)$ reaction. The reaction was first order with respect to each of the reactants. The rate constant depended directly on the hydrogen ion concentration, but it was independent of the initial concentrations of cerium (IV) sulfate and tris-(1,10-phenanthroline)iron(II) sulfate

over a wide range of concentrations.(11) The acidity effect was small. Sulfuric acid from 0.5 M to 0.05 M was used.(12)

The rate of reaction between Tl(III) and tris-(1,10-phenanthroline)iron(II) ion in 2.7 M perchloric acid was observed by George and Irvine(13) in 1954. The rate constant for the reaction was approximately 7.3×10^{-3} liter mole⁻¹ sec⁻¹ at 25°C. when the Tl(III) concentration was 3.6×10^{-2} M and the tris-(1,10-phenanthroline)iron(II) ion concentration was 5.0×10^{-5} M.

PREPARATION AND STANDARDIZATION OF STOCK SOLUTIONS

1. Nitric acid.

Concentrated nitric acid was dissolved in demineralized distilled water. The solution was standardized by titration with standard, carbon-dioxide-free sodium hydroxide. Methyl red was used as the indicator.

Perchloric acid solutions were prepared in the same manner.

2. Tris-(1,10-phenanthroline)iron(II) nitrate.

Iron(II) nitrate nonahydrate(Baker Analyzed) was recrystallized three times from demineralized distilled water. Iron(II) nitrate and three times as many moles of 1,10-phenanthroline were dissolved in dilute nitric acid. The tris-(1,10-phenanthroline)iron(II) nitrate was precipitated by the addition of concentrated sodium nitrate and cooling in a freezer. The solution was filtered, and the precipitate was dissolved in demineralized distilled water. The perchlorate salt of the complex was prepared in a similar manner.(14)

The concentration of the complex was determined spectrophotometrically by use of a Beckman DU Spectrophotometer and published values for the molar absorbtivity. The wavelength of maximum absorbance is 510 $m\mu$, and the molar absorbtivity at this wavelength is 11.1×10^3 .(15)

3. Tris-(1,10-phenanthroline)iron(III) nitrate.

(a.) Tris-(1,10-phenanthroline)iron(II) nitrate was oxidized by the addition of an excess of cerium(IV) sulfate.

(5)

(b.) Tris-(1,10-phenanthroline)iron(II) nitrate was dissolved in dilute sulfuric acid and oxidized with an excess of lead dioxide. The excess lead dioxide and lead sulfate were filtered off. The filtrate was placed in a freezer to precipitate the iron(III) complex. The complex was filtered out of the solution and then dissolved in a small amount of 1 M nitric acid and reprecipitated in a freezer. The precipitate was dissolved in 9 M nitric acid and stored in a freezer in a brown bottle.(14)

Perchlorate solutions of tris-(1,10-phenanthroline)-iron(III) ion were prepared in an analogous manner.

The complex concentration was determined spectrophotometrically at 600 m μ . The cerium oxidized solution cannot be standardized at that wavelength because cerium(IV) also absorbs at that wavelength. The molar absorptivity of the complex at 510 m μ is 300.(5) There is no interference from cerium(IV) at the latter wavelength.

4. Thallium(I) nitrate.

Thallium(I) nitrate(Fisher) was dissolved in hot demineralized distilled water, and it was recrystallized when the solution was cooled. The process was repeated twice. The precipitate was dissolved in dilute nitric acid.

Standardization was accomplished by adding hot concentrated hydrochloric acid to a measured sample of the Tl(I) solution to make the sample 5-8% hydrochloric acid. The acid was heated (40-70°C.) to prevent the precipitation of the thallium(I) chloride and to prevent clogging of the saturated calomel electrode tip. The sample was then titrated potentiometrically with standard potassium bromate. A Beckman Model G pH meter with saturated calomel and platinum electrodes was employed. (16)

5. Thallium(I) perchlorate.

Thallium(I) nitrate (Fisher) was dissolved in hot concentrated perchloric acid and heated at 105-135°C. to remove the nitric acid formed. Thallium(I) perchlorate precipitated when the solution was cooled. The precipitate was recrystallized twice from dilute perchloric acid. (17) The filtrate gave a negative brown ring test for nitrate. The precipitate was dried at 120°C. for an hour. It was then weighed and dissolved in dilute perchloric acid. The solution was standardized by the procedure described for the thallium(I) nitrate.

6. Thallium(III) nitrate.

Thallium(I) nitrate (Fisher) was dissolved in concentrated hydrochloric acid. Thallium(I) chloride precipitated and was suspended in 1 M hydrochloric acid and heated to 60°C. An equivalent amount of potassium bromate was added to the

hot solution to oxidize the thallium(I) to thallium(III). The solution was made basic with concentrated ammonium hydroxide. The thallium(III) hydroxide precipitated and was washed with dilute ammonium hydroxide by decantation until there was no evidence of chloride ion when a sample of the wash solution was added to silver nitrate and nitric acid.(18) The precipitate was dissolved in 9 M nitric acid and stored in a brown bottle in the dark. Thallium(III) perchlorate was prepared in an analogous manner.

To standardize the solution a measured sample was reduced to thallium(I) by bubbling sulfur dioxide through it. The sulfur dioxide reduced the nitrate first. When all the brown vapors were expelled, sulfur dioxide was bubbled into the solution at a moderate rate for an additional twenty minutes. The solution was then boiled for an hour to remove any excess sulfur dioxide(22) and titrated according to the procedure for thallium(I) nitrate.

To determine the hydrogen ion concentration in the thallium(III) nitrate stock solution an one-hundredfold excess of sodium bromide was added to complex the thallium before the solution was titrated with standard sodium hydroxide by using methyl red indicator.(19)

7. Sodium nitrate.

Sodium nitrate(Baker Analyzed) was recrystallized twice and then dissolved in demineralized distilled water. After

being filtered through a fine fritted funnel, the filtrate was boiled gently until small particles appeared on the surface of the liquid. A small amount of water was added to dissolve the solid before the solution was placed in a 60°C. oven for twenty-four hours. The crystals were filtered and left unwashed.(16) Sodium perchlorate prepared in this manner was obtained from James Hoeschele.

The sodium nitrate crystals were dissolved in demineralized distilled water, and the solution was standardized by placing measured aliquots in weighed porcelain crucibles with lids and drying for twenty-four hours at 165°C. with the crucible lids askew. The crucibles were then covered and cooled for thirty minutes in a dessicator before weighing.(19)

8. Potassium bromate.

Potassium bromate(Baker Analyzed) was dried in an oven for twelve hours at 165°C. and then were allowed to stand over concentrated sulfuric acid for an hour before weighing. The weighed potassium bromate was dissolved in demineralized distilled water.

9. Lanthanum(III) nitrate.

C.P. Lanthanum(III) nitrate(Fairmount) was dissolved in demineralized distilled water.

10. Aluminum(III) nitrate.

Reagent grade aluminum(III) nitrate(Baker Analyzed) was dissolved in demineralized distilled water.

11. Strontium(II) nitrate.

Reagent grade strontium(II) nitrate(Baker Analyzed)
was dissolved in demineralized distilled water.

12. Cerium(III) nitrate.

Cerium(III) nitrate(Fisher), reagent grade, was dissolved
in demineralized distilled water.

EXPERIMENTAL PROCEDURE

A thermostated Beckman DU Spectrophotometer was employed to obtain all spectrophotometric data. The kinetic studies were conducted in the presence of oxygen as initial studies in a nitrogen atmosphere showed no variation in the results.

All the reagents used in the kinetic experiments were stored at 25°C. in a thermostated bath for one hour prior to each experiment. The moment at which the tris-(1,10-phenanthroline)iron(II) nitrate or perchlorate was injected into the sample cell was recorded as the initial time, t_0 .

The experiments were conducted by utilizing tris-(1,10-phenanthroline)iron(II) concentrations which were varied within the range $1.21 \times 10^{-4} \text{ M}$ to $6.19 \times 10^{-6} \text{ M}$. The thallium(III) concentrations were varied between $3.90 \times 10^{-2} \text{ M}$ and $2.11 \times 10^{-6} \text{ M}$. The hydrogen concentration range was 2.9 M to 0.5 M .

In preparing the kinetic solutions the thallium(III) was introduced into a four milliliter spectrophotometer cell, one centimeter in width, followed by the addition of the acid. The iron-phenanthroline complex was added at the moment the timing of the reaction was begun. This moment was thirty seconds after the addition of the acid.

To eliminate the possibility of any disappearance of the complex before the thallium(III) was added to the kinetic solution, the acid was added to the thallium(III) solution which was initially 0.5 M in hydrogen ion.

The final volume in the sample cell for each experiment was three milliliters.

The absorbance of the tris-(1,10-phenanthroline)iron(II) ion at 510 m μ was recorded at various time intervals until approximately 90% of the original iron(II) complex had disappeared.

RESULTS AND DISCUSSION

An experiment at the concentrations utilized by George and Irvine, thallium(III) perchlorate = 3.6×10^{-2} M, tris-(1,10-phenanthroline)iron(II) ion = 5.0×10^{-5} M and hydrogen ion = 2.7 M, had a rate constant equal to 7.32×10^{-3} liter mole⁻¹ sec⁻¹. The rate constant reported by George and Irvine (14) was 7.3×10^{-3} liter mole⁻¹ sec⁻¹. The reaction appears to be first order in thallium(III) and first order in tris-(1,10-phenanthroline)iron(II) ion. (Fig.1)

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = k[\text{Fe(phen)}_3^{2+}](\text{Tl}^{3+})$$

$$\ln \frac{[\text{Fe(phen)}_3^{2+}]_t}{(\text{Tl}^{3+})_t} = \frac{[\text{Fe(phen)}_3^{2+}]_0 - 2(\text{Tl}^{3+})_0}{2} kt + \ln \frac{[\text{Fe(phen)}_3^{2+}]_0}{(\text{Tl}^{3+})_0}$$

The above experiments were performed with perchloric acid solutions. At low acid concentrations the perchlorate salt of the iron-phenanthroline complex precipitates upon the addition of either thallium perchlorate or sodium perchlorate. Therefore in all succeeding experiments nitrates were used instead of perchlorates.

In nitrate solutions when the thallium(III) concentration was 4.74×10^{-3} M or larger, the over-all reaction consisted of two concurrent reactions: the dissociation of the complex (first order in complex) and a second order oxidation

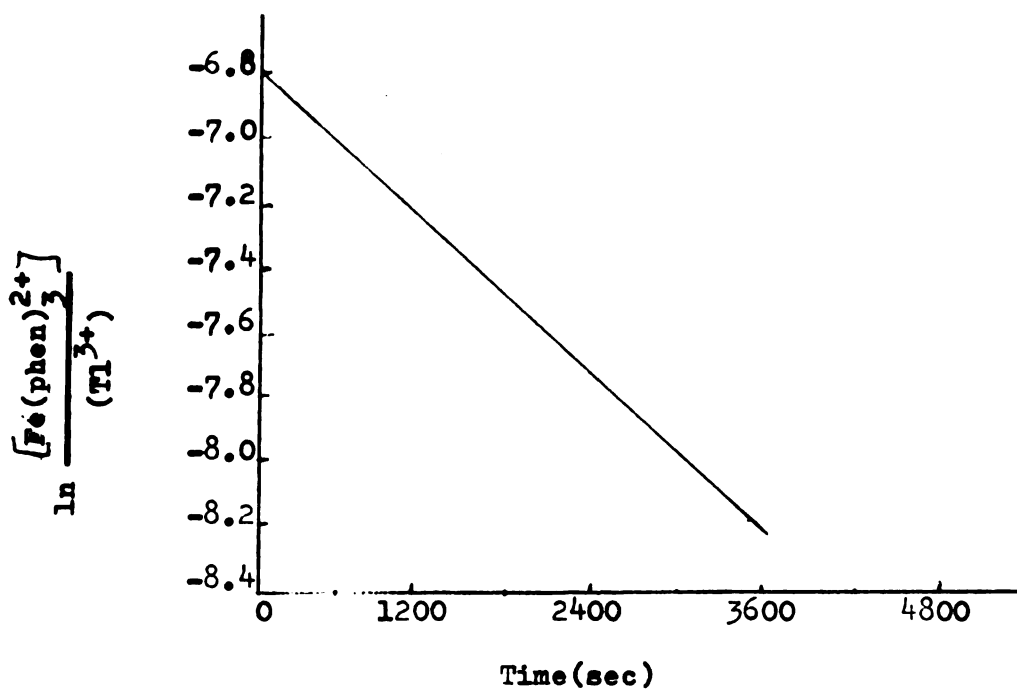
reaction analogous to the oxidation reaction noted in the perchlorate solutions by George and Irvine. (Fig. 2)

$$-\frac{d[\text{Fe(phen)}_3^{2+}]}{dt} = k_{\text{diss}}[\text{Fe(phen)}_3^{2+}] + k_{\text{ox}}[\text{Fe(phen)}_3^{2+}](\text{Tl}^{3+})$$

The two paths were found for a variety of concentrations of the complex when the thallium concentration was $4.74 \times 10^{-3} \text{ M}$, the hydrogen concentration was 1.0 M and the ionic strength was 3.0.

FIGURE 1

Time dependence of $\ln \frac{[\text{Fe(phen)}_3^{2+}]}{(\text{Tl}^{3+})}$ in perchlorate solution.



$$[\text{Fe(phen)}_3^{2+}]_0 = 4.31 \times 10^{-5} \text{ M}$$

$$(\text{Tl}^{3+}) = 3.90 \times 10^{-2} \text{ M}$$

$$(\text{H}^+) = 2.7 \text{ M}$$

$$\mu = 3.0$$

$$\text{Temperature} = 25.0 \pm 0.1^\circ\text{C.}$$

TABLE 1

$[\text{Tl(III)NO}_3] = 4.74 \times 10^{-3} \text{ M}$ Temperature = $25.0 \pm 0.1^\circ\text{C}$.

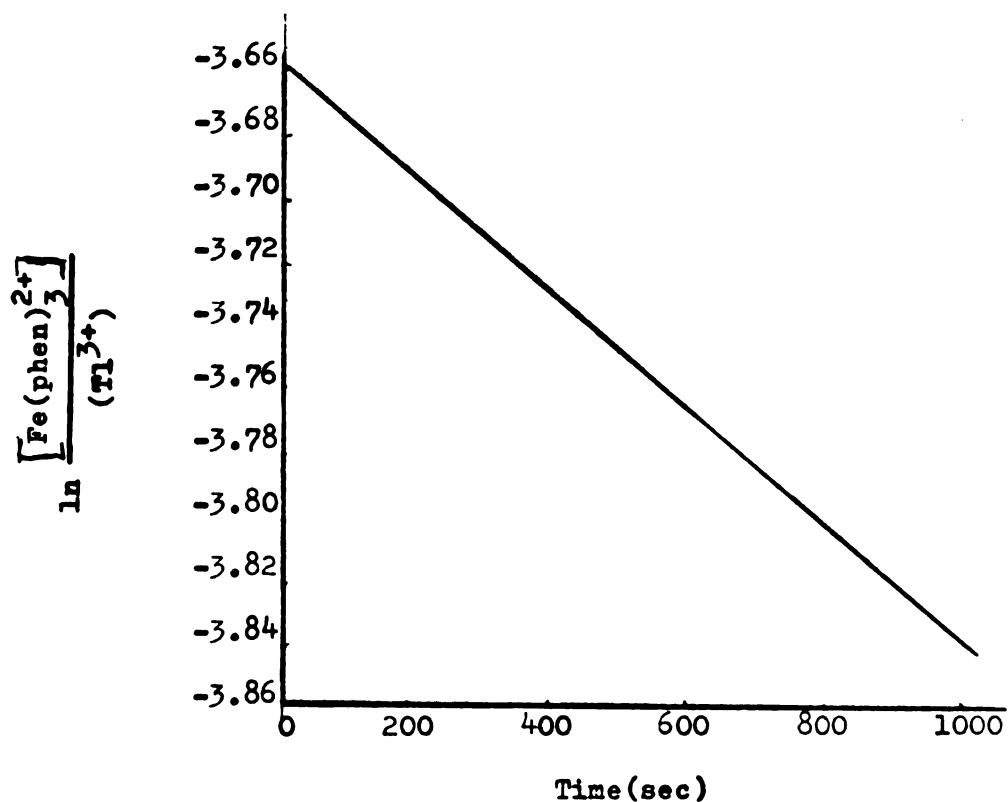
$(\text{H}^+) = 1.0 \text{ M}$

$\mu = 3.0$

| $[\text{Fe(phen)}_3^{2+}] \text{ (M)}$ | $k_{\text{ox}} \text{ (1/mole/sec)}$ | deviation |
|---|--------------------------------------|-----------------------|
| 1.21×10^{-4} | 5.04×10^{-2} | 0.25×10^{-2} |
| 6.00×10^{-5} | 4.69×10^{-2} | 0.10×10^{-2} |
| 5.75×10^{-5} | 4.89×10^{-2} | 0.10×10^{-2} |
| 5.60×10^{-5} | 4.52×10^{-2} | 0.17×10^{-2} |
| 5.30×10^{-5} | 4.56×10^{-2} | 0.13×10^{-2} |
| 3.22×10^{-5} | 4.96×10^{-2} | 0.17×10^{-2} |
| 3.12×10^{-5} | 4.90×10^{-2} | 0.11×10^{-2} |
| 3.12×10^{-5} | 4.93×10^{-2} | 0.14×10^{-2} |
| 2.69×10^{-5} | 4.71×10^{-2} | 0.08×10^{-2} |
| 2.69×10^{-5} | 4.65×10^{-2} | 0.14×10^{-2} |
| average $k_{\text{ox}} = 4.785 \times 10^{-2} \text{ 1/mole/sec}$ | | |
| standard deviation = $0.146 \times 10^{-2} \text{ 1/mole/sec}$ | | |

FIGURE 2

Time dependence of $\ln \frac{[\text{Fe}(\text{phen})_3^{2+}]}{(\text{Tl}^{3+})}$ in nitrate solution.



$$[\text{Fe}(\text{phen})_3^{2+}]_0 = 1.21 \times 10^{-4} \text{ M}$$

$$(\text{Tl}^{3+})_0 = 4.74 \times 10^{-3} \text{ M}$$

$$(\text{H}^+) = 1.0 \text{ M}$$

$$\mu = 3.0$$

$$\text{Temperature} = 25.0 \pm 0.1^\circ\text{C}.$$

* The concentrations have been corrected for the dissociation of the iron complex.

The rate constant for the reaction at the conditions listed in Table 1 is $4.79 \pm 0.15 \times 10^{-2}$ liter mole⁻¹ sec⁻¹. Table 2 gives the corresponding data for the reaction at the same concentrations at 30°C.

TABLE 2

$$[\text{Tl}(\text{NO}_3)_3] = 4.74 \times 10^{-3} \text{ M}$$

$$\text{Temperature} = 30.0 \pm 0.1^\circ\text{C.}$$

$$[\text{H}^+] = 1.0 \text{ M}$$

$$\mu = 3.0$$

| $\text{Fe}(\text{phen})_3^{2+} \text{ (M)}$ | $k_{\text{ox}} \text{ (1/mole}\cdot\text{sec)}$ | deviation | (deviation) ² |
|--|---|-----------|--------------------------|
| 5.75×10^{-5} | 0.515 | 0.13 | 0.0169 |
| 3.16×10^{-5} | 0.562 | 0.34 | 0.1156 |
| 2.68×10^{-5} | 0.524 | 0.04 | 0.0016 |
| 2.53×10^{-5} | 0.536 | 0.08 | 0.0064 |
| 2.16×10^{-5} | 0.502 | 0.26 | 0.0676 |
| average $k_{\text{ox}} = 0.528 \text{ 1/mole}\cdot\text{sec}$ | | | |
| standard deviation = $\pm 0.174 \text{ 1/mole}\cdot\text{sec}$ | | | |

The rate constant for the above reaction is 0.528 ± 0.174 liter mole⁻¹ sec⁻¹.

When the thallium concentration varied below 4.74×10^{-3} moles per liter, the rate of dissociation of the iron complex increased rapidly as the thallium(III) concentration decreased. The data suggest that the thallium(III) acted as a catalyst for the dissociation of the iron-phenanthroline complex. The solutions which contained thallium(III) nitrate in the

concentration range of $4.22 \times 10^{-4} \text{ M}$ to $2.11 \times 10^{-6} \text{ M}$ did not turn blue during the course of the reaction, which indicated that no tris-(1,10-phenanthroline)iron(III) ions were formed. At these low thallium(III) concentrations the rate increased very rapidly with a decrease in the thallium(III) concentration.

These results seemed to indicate that the dissociation reaction rate was much greater than the rate of the oxidation process. A series of experiments using trivalent ions which would not oxidize the iron-phenanthroline complex were performed to obtain data on the dissociation rate which would assist in the interpretation of the data obtained for the two concurrent reactions. The data obtained using Al(III), Ce(III) and La(III) are tabulated in Table 3.

TABLE 3

$$[\text{Fe}(\text{phen})_3^{2+}] = 6.9 \times 10^{-5} \text{ M} \quad \text{Temperature} = 25.0 \pm 0.1^\circ\text{C.}$$

$$(\text{H}^+) = 1.0 \text{ M}$$

$$(\text{M}^{3+}) = 4.74 \times 10^{-4} \text{ M}$$

$$\mu = 3.0$$

| Ion used | Rate (mole/ liter/ sec) experimental-initial |
|------------------|---|
| Al ³⁺ | 7.08×10^{-8} |
| Ce ³⁺ | 6.88×10^{-8} |
| La ³⁺ | 7.14×10^{-8} |

These rates are analogous to those found for the thallium(III)-tris-(1,10-phenanthroline)iron(II) nitrate kinetic solutions. An experiment was then performed to determine whether strontium(II) behaved in a similar manner. As the concentration of strontium(II) increased, the rate of the disappearance of the iron-phenanthroline complex increased. (Table 4). Further studies on the lanthanum(III)-iron-phenanthroline system showed that the rate of disappearance of the iron complex increased as the lanthanum(III) concentration decreased (Table 5).

TABLE 4

$$[\text{Fe}(\text{phen})_3^{2+}] = 5.75 \times 10^{-5} \text{ M} \quad \text{Temperature} = 25.0 \pm 0.1^\circ\text{C.}$$

$$(\text{H}^+) = 1.0 \text{ M}$$

$$\mu = 3.0$$

| (Sr^{2+}) (M) | Rate (mole/ liter/ sec) experimental-initial |
|--------------------------|---|
| 2.37×10^{-4} | 7.0×10^{-8} |
| 1.19×10^{-3} | 9.42×10^{-8} |
| 4.74×10^{-3} | 9.17×10^{-8} |

TABLE 5

 $(H^+) = 1.0 \text{ M}$ Temperature = $25.0 \pm 0.1 \text{ M}$ $\mu = 3.0$

| $[Fe(phen)_3^{2+}]$ ($\underline{M} \times 10^5$) | (La^{3+}) (\underline{M}) | Initial Rate (mole/liter/sec) | k_1 (mole/ liter/ sec) | k_2 (sec^{-1}) |
|--|------------------------------------|----------------------------------|-----------------------------------|-------------------------|
| 5.75 | 4.74×10^{-3} | 1.06×10^{-7} | 0.0877 | 0.0595 |
| 2.78 | 4.74×10^{-3} | 4.80×10^{-8} | 0.0885 | 0.0595 |
| 1.67 | 4.74×10^{-3} | 2.28×10^{-8} | 0.0855 | 0.0595 |
| 7.00 | 9.48×10^{-4} | 9.00×10^{-8} | 0.0815 | 0.0595 |
| 6.90 | 4.74×10^{-4} | 7.14×10^{-8} | 0.0733 | 0.0595 |
| 6.10 | 4.74×10^{-4} | 8.07×10^{-8} | 0.0866 | 0.0595 |
| 2.85 | 4.74×10^{-4} | 3.97×10^{-8} | 0.0845 | 0.0595 |
| 2.22 | 4.74×10^{-4} | 5.38×10^{-8} | 0.1015 | 0.0595 |
| 7.00 | 9.48×10^{-5} | 9.00×10^{-8} | 0.0850 | 0.0595 |
| 7.20 | 4.74×10^{-5} | 1.04×10^{-7} | 0.0790 | 0.0595 |
| 6.95 | 4.74×10^{-5} | 1.94×10^{-7} | 0.0990 | 0.0595 |
| 3.45 | 4.74×10^{-5} | 8.50×10^{-8} | 0.1013 | 0.0595 |
| 1.98 | 4.74×10^{-5} | 3.71×10^{-8} | 0.1000 | 0.0595 |
| average $k_1 = 0.0887$ mole/liter/sec | | | | |
| standard deviation = 0.0084 mole/liter/sec | | | | |

The rate constant were calculated from the equation

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

which in integral form (see Appendix 1) is

$$[\text{Fe(phen)}_3^{2+}]_t = -k_1/k_2 + \{[\text{Fe(phen)}_3^{2+}]_0 + k_1/k_2\} e^{-k_2 t}.$$

The values for k_1 and k_2 are 0.0887 ± 0.0084 mole liter⁻¹sec⁻¹ and 0.0595 sec⁻¹, respectively.

A comparison of the rates for reactions in which low concentrations of thallium(III) are used with rates for reactions where lanthanum(III) was utilized (see Appendix 3) showed a good correlation between the two sets of rates. The thallium could be catalyzing the dissociation of the iron complex, but the hydrolysis of the thallium(III) probably complicates the reaction at low thallium and hydrogen ion concentrations and makes the mathematical interpretation of the results uncertain.

It appears that the thallium catalyzed dissociation may also consist of two concurrent steps; one first order in iron complex and the second zero order.

The reaction rate for both the thallium(III) and the lanthanum(III) reactions with tris-(1,10-phenanthroline)iron(II) ion were accelerated as the hydrogen ion concentration was increased at high acidities. When the acid concentration was

lowered below 0.7 M, the rate appeared to increase with decreasing hydrogen ion concentration.

TABLE 6

$$[\text{Fe}(\text{phen})_3^{2+}] = 6.00 \times 10^{-5} \text{ M}$$

$$\text{Temperature} = 25.0 \pm 0.1^\circ\text{C.}$$

$$(\text{Tl}^{3+}) = 4.74 \times 10^{-3} \text{ M}$$

$$(\text{La}^{3+}) = 4.74 \times 10^{-3} \text{ M}$$

$$\mu = 3.0$$

| (H ⁺) (M) | Initial Rate, experimental (mole/liter/sec) | |
|-----------------------|--|-------------------------|
| | Tl(III) | La(III) |
| 2.9 | 2.69 x 10 ⁻⁷ | |
| 2.7 | 1.96 x 10 ⁻⁷ | |
| 2.5 | 2.07 x 10 ⁻⁷ | |
| 2.0 | 1.34 x 10 ⁻⁷ | 5.56 x 10 ⁻⁷ |
| 1.5 | 7.87 x 10 ⁻⁸ | 1.39 x 10 ⁻⁷ |
| 1.3 | 1.04 x 10 ⁻⁷ | |
| 1.2 | 6.57 x 10 ⁻⁸ | |
| 1.0 | 1.86 x 10 ⁻⁸ | 7.14 x 10 ⁻⁸ |
| 0.7 | 2.58 x 10 ⁻⁸ | |
| 0.5 | 9.56 x 10 ⁻⁹ | 8.84 x 10 ⁻⁸ |

The increase in the rate of disappearance of the iron-phenanthroline complex with the increase in acid strength was much greater in the thallium case than in the lanthanum case. Since the tris-(1,10-phenanthroline)iron(II) ion concentration was equal in both cases, the increase could be due to the oxidation of the iron complex by thallium. The increase in the oxidation rate with an increase in hydrogen ion concentration might be caused by a smaller degree of hydrolysis of the thallium(III) ion-- the oxidation probably involves the Tl^{3+} species.

George and Irvine(13) reported that the rate for the thallium(III)-tris-(1,10-phenanthroline)iron(II) ion was approximately inversely proportional to the first power of the hydrogen ion concentration. This relationship is not found in the present work. In reactions where there was proof of the oxidation of the complex, the rate increased as the hydrogen ion concentration increased,

The above result serves to cast doubt on the assumption of George and Irvine that the chief species reacting with the complex ion reducing agent is TlO^+ . At low acid concentrations when the disappearance of the iron complex was complete, it was noted that there was still $Tl(III)$ present in the solution. The Tl^{3+} concentration may be too small to oxidize the iron complex, and/or the low Tl^{3+} concentration may catalyze the dissociation reaction greatly.

A study of the effect of various univalent ions was performed(5) by adding varied amounts of hydrogen ion, potassium ion, lithium ion and nitrate ion to a solution of tris-(1,10-phenanthroline)iron(II) ion which was 2.5×10^{-5} M. A simultaneous increase in the hydrogen and nitrate concentrations caused an increase in the rate of dissociation. The same result was obtained with lithium nitrate, but the addition of larger amounts of potassium nitrate caused a slight increase in the rate. These rate variations were small compared to those noted for the addition of lanthanum(III) or thallium(III) nitrate to the iron-phenanthroline complex. This work done by Dickens, Basolo and Neumann gave a rate constant of approximately $7.5 \times 10^{-5} \text{ sec}^{-1}$ for the iron complex dissociation.

The present experiments that were performed by using perchlorate solutions give results analogous to the nitrate data. The perchlorate results must be weighted rather lightly since precipitation appeared to occur during the kinetic study of most of the solutions. Only in the 2.7 M acid solution precipitation definitely did not occur.(See Appendix 4)

These experiments except for the hydrogen ion dependence seem to support the work of George and Irvine when large concentrations of thallium(III) are used, and it can be expected that the thallium(III) concentration will be nearly constant throughout the experiment. Under these conditions oxidation of the tris-(1,10-phenanthroline)iron(II) ion appears to occur,

but dissociation of the complex seems to occur concurrently. This latter supposition was not considered by George and Irvine.

At low thallium(III) concentrations there appears to be little or no oxidation. The principal reaction seems to be a rapid dissociation of the complex which is catalyzed by the unhydrolyzed trivalent ion.

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APPENDIX 1

Let $[\text{Fe}(\text{phen})_3^{2+}] = y$; then $-\frac{dy}{dt} = k_1 + k_2 y$

$$\frac{d(y e^{k_2 t})}{dt} = -k_1 e^{k_2 t}$$

$$y e^{k_2 t} = -(k_1/k_2) e^{k_2 t} + c$$

$$\text{When } t = 0, c = y_0 + (k_1/k_2) e^{-k_2 t}$$

$$y = -k_1/k_2 + (y_0 + k_1/k_2) e^{-k_2 t}$$

APPENDIX 2

 $(H^+) = 1.0 \text{ M}$ $\mu = 3.0$ Temperature = $25.0 \pm 0.1^\circ\text{C}$.

| $[\text{Fe}(\text{phen})_3^{2+}] \text{ (M)}$ | $(\text{Tl}^{3+}) \text{ (M)}$ | $(\text{La}^{3+}) \text{ (M)}$ | Initial Rate, experimental (mole/liter/sec) |
|---|--------------------------------|--------------------------------|---|
| 5.57×10^{-5} | 2.11×10^{-4} | | 1.95×10^{-7} |
| 6.16×10^{-5} | 4.22×10^{-5} | | 1.21×10^{-7} |
| 6.00×10^{-5} | 2.11×10^{-5} | | 3.24×10^{-7} |
| 6.20×10^{-5} | 4.22×10^{-6} | | 3.13×10^{-7} |
| 5.75×10^{-5} | 2.11×10^{-6} | | 2.61×10^{-7} |
| 7.00×10^{-5} | | 9.48×10^{-4} | 9.00×10^{-8} |
| 6.90×10^{-5} | | 4.74×10^{-4} | 7.14×10^{-8} |
| 7.00×10^{-5} | | 9.48×10^{-5} | 1.35×10^{-7} |
| 7.20×10^{-5} | | 4.74×10^{-5} | 1.04×10^{-7} |

APPENDIX 3

$$[\text{Fe}(\text{phen})_3^{2+}] = 5.75 \times 10^{-5} \text{ M}$$

$$(\text{La}^{3+}) = 4.74 \times 10^{-3} \text{ M}$$

$$(\text{H}^+) = 1.0 \text{ M}$$

$$\mu = 3.0$$

| Temperature (°C.) | Initial Rate, experimental (mole/liter/sec) |
|-------------------|--|
| 35.0 | 1.05×10^{-7} |
| 30.0 | 9.00×10^{-8} |
| 20.0 | 5.54×10^{-8} |

APPENDIX 4

Perchlorate Data

$(H^+) = 0.10 \text{ M}$

Temperature = $25.0 \pm 0.1^\circ\text{C}$.

$\mu = 3.0$

| $[Fe(phen)_3^{2+}] \text{ (M)}$ | $(Ti^{3+}) \text{ (M)}$ | Initial Rate, experimental (mole/liter/sec) |
|---------------------------------|-------------------------|--|
| 1.07×10^{-4} | 1.07×10^{-4} | 3.28×10^{-8} |
| 1.64×10^{-4} | 1.46×10^{-4} | 2.67×10^{-7} |
| 1.07×10^{-4} | 9.70×10^{-3} | 9.60×10^{-9} |
| 2.57×10^{-5} | 1.80×10^{-3} | 3.69×10^{-8} |

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