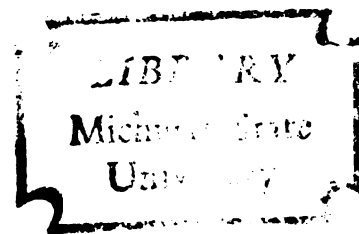


THE KINETICS OF THE OXIDATION OF
SUBSTITUTED 2,2'-BIPYRIDINE AND
1,10-PHENANTHROLINE COMPLEXES OF
IRON(II) WITH PEROXYDISULFATE IONS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
SAROJA N. RAMAN
1968



This is to certify that the

thesis entitled

THE KINETICS OF THE OXIDATION OF SUBSTITUTED
2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES
OF IRON(II) WITH PEROXYDISULFATE ION
presented by

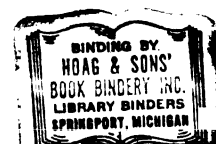
Saroja N. Raman

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker
Major professor

Date July 12, 1968

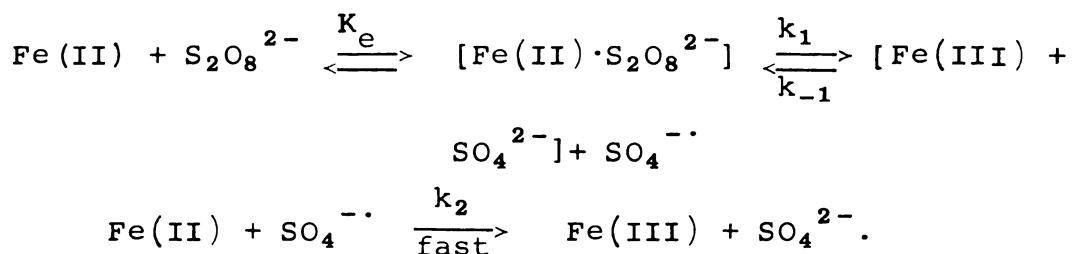


ABSTRACT

THE KINETICS OF THE OXIDATION OF SUBSTITUTED 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF IRON(II) WITH PEROXYDISULFATE IONS

by Saroja N. Raman

The kinetics of oxidation of 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, 5-chloro-, 5-nitro- and 5-methyl-1,10-phenanthroline complexes of iron(II) with peroxydisulfate have been studied. The complexes are oxidized according to the mechanism



The reverse step is formulated as a bimolecular step involving the $\text{Fe(III)}\text{-SO}_4^{2-}$ ion pair and sulfate radical ion. The forward rate constants, the equilibrium constants and the activation parameters are reported.

The formation of sulfate radical ion in the rate determining step of the reaction has been proved from the study of the effect of alcohol on the rate of oxidation of the tris-(2,2'-bipyridine)-iron(II) complex. At high concentrations of sulfate ions, the complex cations form ion pairs, which seem to be the principal species undergoing oxidation under these conditions.

There is a reasonable linear relationship between the free energy of activation and the standard free energy of the rate determining step, for these complexes. Such a relationship is also found between the pK_a and the Hammett substituent constants of the ligands and the logarithm of the forward rate constants.

THE KINETICS OF THE OXIDATION OF SUBSTITUTED
2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES
OF IRON(II) WITH PEROXYDISULFATE IONS

By

Saroja N. Raman

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1968

G. 520-4
1/5/69

ACKNOWLEDGMENTS

The author is very grateful to Professor Carl H. Brubaker, for his continued assistance and encouragement throughout the work, which made this thesis possible. No words are adequate to express her deep gratitude to her husband K. V. Raman and to her daughter Kalpana, for their patience and understanding.

The financial support from the Atomic Energy Commission is gratefully acknowledged.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. HISTORICAL	12
III. EXPERIMENTAL	18
A. Preparation of Reagents	18
B. Analytical Methods	19
C. Procedure	22
D. Errors	24
IV. THEORETICAL	26
V. RESULTS	31
Determination of the Rate Constants	31
A. Effect of Alcohol on the Reaction	40
B. Effect of Sulfate Ions	43
C. Activation Parameters	46
D. Relationship Between ΔG^* and ΔG^0	49
E. Relationship Between the Rate Constants and the pK_a s of the Monoprotonated Ligands and the Hammett Substituent Constants	52
F. Errors	52
VI. DISCUSSION	56
A. Mechanism	56
B. Role of Alcohol	64
C. Mode of Electron Transfer	66
D. Activation Parameters	67
E. Effect of Substituents	68
LITERATURE CITED	70
APPENDIX	76

LIST OF TABLES

TABLE		Page
I.	Molar absorptivities of the substituted 1,10-phenanthroline and 2,2'-bipyridine complexes of iron(II) and iron(III)	20
II.	Dependence of the second order rate constants on the concentration of peroxydisulfate . . .	32
III.	Rate constants for the complex perchlorates .	34
IV.	Forward rate constants and equilibrium constants	39
V.	Values of the ratio $\frac{k_{-1}}{k_2}$	42
VI.	Rates of reaction, in the presence of excess <u>tris</u> -(2,2'-bipyridine)-iron(II) sulfate . . .	42
VII.	Effect of alcohol on the rate of the reaction	44
VIII.	Effect of sulfate ion concentration on the rates	45
IX.	Activation parameters	50

LIST OF FIGURES

FIGURE	Page
1. Graph of $1/k_{ob}$ <u>versus</u> peroxydisulfate concentration for <u>tris</u> -(2,2'-Bipyridine)-iron(II) sulfate	36
2. Graph of $1/k_{ob}$ <u>versus</u> peroxydisulfate concentration for <u>tris</u> -(4,4'-Dimethyl-2,2'-bipyridine)-iron(II) sulfate	36
3. Graph of $1/k_{ob}$ <u>versus</u> peroxydisulfate concentration for <u>tris</u> -(1,10-Phenanthroline)-iron(II) sulfate	37
4. Graph of $1/k_{ob}$ <u>versus</u> peroxydisulfate concentration for <u>tris</u> -(5-Methyl-1,10-phenanthroline)-iron(II) sulfate	38
5. Graph of $1/k_{ob}$ <u>versus</u> the peroxydisulfate concentration for <u>tris</u> -(5-Nitro-1,10-phenanthroline)-iron(II) sulfate	38
6. Graph of $1/k_{ob}$ <u>versus</u> the peroxydisulfate concentration for <u>tris</u> -(5-Chloro-1,10-phenanthroline)-iron(II) sulfate	38
7. Probable occurrence of the reverse reaction. Graph of $-[Fe(II)]_t - [Fe(II)]_{eq}$ <u>versus</u> time for <u>tris</u> -(1,10-phenanthroline)-iron(II) sulfate	41
8. Effect of sulfate ion concentration on the rate for <u>tris</u> -(2,2'-Bipyridine)-iron(II) sulfate	47
9. Arrhenius plot. Graph of $\log k_f$ <u>versus</u> $1/T$	48
10. Relation between the free energy of activation and the standard free energy change of the oxidation-reduction step	51
11. Relation between the forward rate constants and the pK_a 's of the ligands	53

LIST OF FIGURES (Cont.)

FIGURE	Page
12. Relation between the forward rate constants and the Hammett substituent constants (σ) of the ligands	54

INTRODUCTION

There has been extensive study during the past fifteen years in the field of kinetics and mechanisms of inorganic reactions in solution. The reactions studied can be grouped into two major classes: (1) Ligand substitution reactions^{1,2} and (2) electron transfer reactions which include both oxidation-reduction and simple electron exchange processes, which do not involve a net chemical reaction.^{3,22,42,52,94,95}

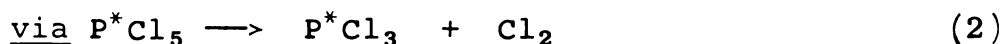
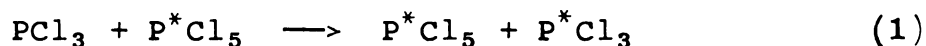
A great majority of the early work was concerned only with the evaluation of stoichiometry and thermodynamics and it is only in the last fifteen years that the area of the mechanisms of reactions has received serious attention. The mechanisms are evaluated from an experimental knowledge of the form of the rate law for the reaction in question and also from the knowledge of other factors such as the influence of added substances, dielectric constant and ionic strength of the medium on the rate of the reaction.

But the more fundamental question of just how the electrons are transferred from reducing to oxidizing agents, in reactions which take place in solutions is yet to be answered fully.²² Much of the current work in the field of oxidation-reduction is concerned with an attempt to answer this question.

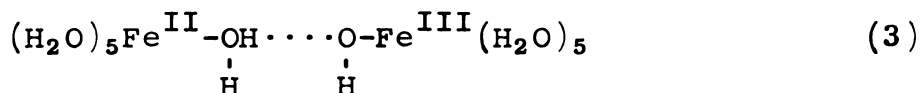
A large body of data from the rates of reactions, thermodynamic parameters and other important evidence concerning the participation or nonparticipation of certain species in

the reaction, has lead to the postulation of three possible pathways for effecting electron transfer in reactions in solution.^{3,22,42,52,94,95}

Effective transfer of electrons may result from an atom or group transfer such as is found in one path for the exchange reaction³⁵



A sodium atom transfer has been proved by E.S.R. measurement in the case of electron transfer to benzophenone from its sodium ketyl.¹ Similarly an H atom transfer is supposed to be involved in the exchange between Fe^{2+} and Fe^{3+} in water.⁵⁷



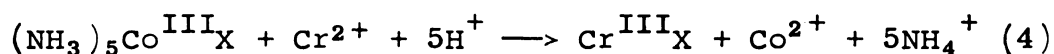
There seems to be no doubt that atom, radical or molecule transfer does occur in some systems and accounts for the change in oxidation states of the participating species. But it is not clear how general such a mechanism may be for solution reactions.

More prevalent are the other two models for electron transfer designated broadly as the "outer sphere" and "inner sphere" mechanisms. In reactions which are supposed to proceed by an outer sphere mechanism^{31,89,93,106} electron transfer occurs through an extended activated complex or outer sphere complex, in which the first coordination shell

of each metal ion is presumably intact. The evidence for this type of mechanism is usually the rate law corresponding to an activated complex containing all the ligands in the first coordination shells of both central atoms [e.g. The rate law for the electron exchange between Co(II) and Co(III) complexes of ethylenediamine is of the form: Rate of exchange = $k [\text{Co}^{\text{II}}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{Co}^{\text{III}}(\text{C}_2\text{H}_8\text{N}_2)_3]$ and/or the demonstration that electron transfer is faster than substitution into the coordination shell of either of the reactants. For these systems, orbital overlap for the two ions is small, so that the frequency of electronic transition is small and there is no substantial binding between the two exchanging centers. The reactions in this class cover a wide range of rates from $k = 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$ for the electron exchange between $\text{Co}^{\text{II}}(\text{NH}_3)_6$ and $\text{Co}^{\text{III}}(\text{NH}_3)_6$ to $k = 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ for systems like $\text{Fe}^{\text{II}}(\text{Ph})_3$ and $\text{Fe}^{\text{III}}(\text{Ph})_3$.^{37,93} In general, metal ions surrounded by unsaturated or large polarizable ligands such as orthophenanthroline, bipyridine, cyanide etc. exchange electrons faster.

In the case of inner sphere reactions, electron transfer is preceded by substitution into the coordination shell of one of the ions with the formation of a bridged species in the transition state or even an intermediate⁵¹ in which the two metal ions are linked by a common ligand. In such cases, there is a strong interaction of the orbitals and interpenetration of the coordination spheres. A significant body of work has been done by Taube and coworkers with

$(\text{NH}_3)_5\text{Co}^{\text{III}}\text{X}$ plus reducing agents such as $\text{Cr}(\text{II})$ in aqueous solutions, where X is H_2O , OH^- , Cl^- , OAc^- , (H-succinate), (H-phthalate), (Me-fumarate), etc. $\text{Cr}(\text{III})$ and $\text{Co}(\text{III})$ are inert and in many cases they have been able to prove the formation of a bridged intermediate by the presence of the X group in the coordination sphere of the $\text{Cr}(\text{III})$ formed during the reaction.



The rates of inner sphere reactions are very sensitive to the nature of the bridging group, reflecting the essential role of the latter in the electron transfer process. Thus there is a 10^6 fold variation in the rate of oxidation of $\text{Cr}(\text{II})$ by $\text{Co}(\text{NH}_3)_5\text{X}$, when the nature of bridging ligand is varied.

In the outer sphere mechanism, transfer of electrons proceeds through a quantum mechanical barrier penetration. Such systems lend themselves to an exhaustive theoretical analysis and Marcus^{73,74,75,77} has successfully derived a quantitative expression for the a priori prediction of the rate constants in such reactions. Other theories include one by R. J. Marcus, Zwolinski and Eyring⁷⁸ in which an experimental system is necessary for the calculation of parameters. Hush⁵⁸ has derived an adiabatic theory which gives essentially the same result as that of Marcus. Review of the various theories has been made by Marcus⁷⁶

The theoretical rate constant according to Marcus' theory can be obtained as follows:⁷⁴

$$k = Z e^{-\Delta G^*/RT} \quad (5)$$

where k is the rate constant, ΔG^* is the free energy of activation, Z is the collision frequency of (hypothetical) uncharged species in solution. ΔG^* is comprised of three different energy terms: Standard free energy of the oxidation-reduction step, the coulombic interaction of the ionic charges of the reactants and products, and the energy for the rearrangement of the inner and outer spheres of the charged reactants. ($\Delta G^* = \Delta G^\ddagger - 2.8 \text{ k cal}$)

$$\Delta G^* = w + m^2 \lambda \quad (6)$$

where

$$m = -\left[\frac{1}{2} + \frac{\Delta G^0 + w^p - w}{\lambda} \right] \quad (7)$$

where w is the work needed to bring the two reactants together and w^p the work needed for separating the products. ΔG^0 is the standard free energy of the elementary electron transfer step in the electrolytic medium under consideration. λ is the reorganization term and includes the effect of changes in bond distances and bond angles in the inner coordination sphere of each reactant and the solvent reorganization around the charged species.

$$\lambda = \lambda_{\text{outer}} + \lambda_{\text{inner}}$$

λ_{outer} depends on the size and shape of the reactants.

$$\lambda_0 = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{\eta^2} - \frac{1}{D_s} \right) (\Delta e)^2 \quad (8)$$

$$\lambda_i = \sum_j \frac{k_j k_j^p}{k_j + k_j^p} (\Delta q_j^0)^2 \quad (9)$$

where a_1 and a_2 are the radii of the spherical particles undergoing reaction, r is the mean distance between the centers of the activated complex $(a_1 + a_2)$. η and D_s are the refractive index and static dielectric constant respectively, (Δe) is the number of electrons transferred, k_j , k_j^p are the force constants of the j^{th} vibrational coordinate for a species as reactant and product respectively, Δq_j^0 is the change in the bond distance in the inner coordination sphere of each reactant. To determine λ_i , the summation is over the j^{th} normal modes of each reactant and over all bonds involved in a particular mode.

If $\frac{\Delta G^0 + w^p - w}{\lambda}$ is small, $\Delta G^* \approx \frac{w + w^p}{2} + \frac{\lambda}{4} + \frac{\Delta G^0}{2}$ (10)

This is the key expression around which interest has centered for the past ten years. If for a series of reactions the coulombic and reorganization energy are constant and the only parameter varied is ΔG^0 , then a plot of ΔG^* versus ΔG^0 should be a straight line with a slope of 0.5.

Sutin and coworkers have made this type of verification of Marcus' theory. They have studied the oxidation of Fe(II) phenanthroline complexes with Ce(IV)^{26,36}, and Mn(III)³⁴ and the reduction of Fe(III) complexes with Fe(II) and have obtained a slope⁴¹ of 0.5 for the plot of ΔG^* versus ΔG^0 which has proved as an important experimental verification of Marcus' theory.

The exact nature of electron transfer in the inner sphere mechanism is not completely settled. The bridging process may occur with two different results; merely to hold the reactants together in similar environments and in proximity until some other process such as electron tunnelling can occur⁷², or to serve as a path for electron conduction⁵³. In either case, the Franck-Condon principle could be operative and the transfer of electrons would occur after the environments of the two bridged species has readjusted to such an extent that coordination number and bond distances would be intermediate between the initial and final positions for each species.

Libby⁷² favors the idea that bridge mechanisms operate simply to connect the reactants, allow them to satisfy Franck-Condon principle and permit tunnelling transfer to take place. He has rationalized most of the results of Taube's reactions on the basis of direct transfer, but there are instances where a facilitation of conduction of electrons may be the consequence of bridge formation. This mechanism seems obvious at least in the Taube reaction when X is nicotinamide or isonicotinamide⁸². The formation of an amide-bound Cr^{III} -nicotinamide complex has been proved by Nordmeyer and Taube⁸² which shows that Cr^{2+} attacks the Co(III) complex at a remote amide oxygen. Since the cobalt atoms are coordinated to the pyridinyl nitrogen, in both cases the ring electron must have been transmitted through the pyridine ring. Wang's work⁹⁷ on the oxidation of

cytochrome C also demonstrates electron conduction through 4,4'-bipyridine bridges. According to Brubaker²² both mechanisms should be possible depending on the nature of the reaction and it is unlikely that either mechanism will be found completely general.

The tris complexes of phenanthroline, bipyridine and their variously substituted derivatives with transition metals like osmium, ruthenium and iron form a convenient and interesting group of compounds from a standpoint of kinetic studies. They form stable nonlabile complexes which dissociate only slowly in acidic or alkaline medium!^{11,17,23,24,33} These complexes have very strong absorption bands in the visible region of the spectrum, and are ideally suited for spectrophotometric work. The ligands exhibit a wide range of pK_a values and so the complexes differ in their stabilities and the metal complexes cover a wide range of oxidation-reduction potentials.

The nonlabile nature of the complexes guarantees that the inner coordination sphere is held intact during oxidation-reduction reactions and so may be conducive to an electron transfer through the outer sphere mechanism. Further there is no change in geometry and only a small change in bond lengths in the two oxidation states, which should lower the reorganization energy. Kinetic studies with extensively π bonded systems like phenanthroline and bipyridine tend to indicate that a large degree of delocalization of the electrons in these systems may be favorable to a tunnelling

mechanism.⁵² Hence, the idea of working with the Fe(II) system seemed very promising and interesting to test Marcus' outer sphere theory.

The wide range of pK_a values of the ligands enables one to seek a correlation between the rate constants and σ , the substituent constant of the Hammett equation.⁶²

$$\log\left(\frac{k_s}{k_0}\right) = \sigma\rho \quad (11)$$

where k_s and k_0 are the equilibrium constants or the rate constants for a series of reactions involving the unsubstituted and substituted (meta or para) derivatives of the benzene ring. σ is the substituent constant and depends solely on the nature and position of the substituent. σ is obtained directly by measuring the effect of that substituent on the ionization constant of benzoic acid in water at 25°.

$$\sigma = \log \left[\frac{K_{X-C_6H_4COOH}}{K_{C_6H_5COOH}} \right] \quad (12)$$

where $K_{X-C_6H_4COOH}$ and $K_{C_6H_5COOH}$ are the ionization constants for the substituted and unsubstituted benzoic acids. ρ is a reaction constant and depends on the nature of the reaction. The Hammett equation provides a quantitative relation between the nature of the substituent and the reactivity of a side chain.

A large variation in the standard oxidation-reduction potential is ideal in any investigation of Marcus' theory

since this is a direct measure of the standard free energy change of the system.

$$-\Delta G^0 = RT \ln K = nFE^0 \quad (13)$$

In a series of oxidation-reduction reactions, if the coulombic and the reorganization energy are held constant, the energy of activation is directly related to ΔG^0 , for an outer sphere electron transfer. The Fe(II) system fulfills this condition as evidenced from the work of Sutin and coworkers^{26,34,36,41}

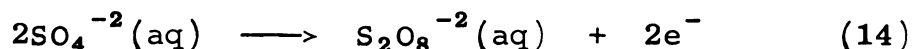
In the present investigation, Tl(III) was meant to be used as an oxidizing agent. Tl(III) is especially interesting because its reduction involves a two-electron transfer and it is not yet established conclusively whether the chemical reduction takes place via two, one-electron steps or by a concerted two-electron transfer, although the electrochemical reduction has been proved to be two one-electron steps.⁷⁴ Much chemical evidence, also points to two, one-electron transfer steps in chemical reactions.^{7,54} Theoretical calculation of the exchange rate of Tl(I) - Tl(III), from the Marcus theory, seems to agree with this.⁷⁴ A similar calculation for the Fe(II) — Tl(III) system, however, gives a low value for the rate as compared to the experimental value. It was hoped that the reaction of Tl(III) with the Fe(II) complexes might lead to some categorical proof of either mechanism. George and Irvine⁴⁸ have reported the rate constant for the oxidation of tris(phenanthroline)iron(II) with Tl(III) in a 2 M HClO₄ medium at a

Tl(III) concentration of 3.5×10^{-2} M. In the present investigation, it was found that under conditions of high acidity, which is essential for preventing the hydrolysis of Tl(III), the acid dissociation of the Fe(II) complexes was fast enough to compete with the oxidation⁹². Irvine⁵⁹ later reported that the oxidation takes place irreversibly which probably suggests that considerable hydrolysis of the compound had occurred in his studies. Extensive hydrolysis was found to occur in the oxidation of tris bipyridine iron(II) complex with Tl^{3+} in 2 M HClO_4 .⁸⁷ Hence, the study was abandoned and peroxydisulfate was chosen as the oxidant since it showed a reasonable rate of oxidation of the iron(II) complexes.

With peroxydisulfate, the oxidation involves breaking up of the peroxide bridge and probably no categorical postulation as regards the mode of electron transfer can be made. The simplified assumption that $(\Delta G^0 + w^p - w)/\lambda$ is small, in the derivation of $\Delta G^* = w + w^p/2 + \lambda/4 + \Delta G^0/2$, may or may not be true. Even if it is, the reactions may not all have similar magnitudes for the λ term (see the discussion in the final chapter). Hence, only a trend can be looked for in the change of ΔG^* versus ΔG^0 . Further complications with the peroxydisulfate system, which are described in the later chapters have added to the difficulty; however, a reasonable straight line with ΔG^* versus ΔG^0 has been obtained.

HISTORICAL

Peroxydisulfate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation-reduction potential for the reaction:



is estimated to be $-2.01 \text{ v.}^{2,71}$ Although it is a two-electron oxidizing agent, in a majority of reactions $\text{S}_2\text{O}_8^{2-}$ ion undergoes either a one-electron reduction with the formation of one sulfate radical ion or a fission of the O-O bond to form two sulfate radical ions. The highly reactive sulfate radical ion may further undergo reactions with the solvent or with various substrates present in the solution. In some cases, the one-electron oxidation product of the substrate may be a reactive intermediate, which may further react with the solvent or other substrates present in the solution, or the peroxydisulfate ion itself. The best example for this is the reaction of $\text{S}_2\text{O}_8^{2-}$ with Fe^{2+} ions in the presence of ethyl alcohol.⁶⁸

One of the most extensively investigated areas in the chemistry of peroxydisulfate ion is its use in organic polymerization reactions. The sulfate radical ion produced by reacting $\text{S}_2\text{O}_8^{2-}$ with a metal ion such as Fe(II) is able to induce oxidations and polymerizations in organic substances and its presence has been confirmed by the incorporation of ^{35}S from labelled peroxydisulfate into polymer

chains.^{40,68,70,81,91} The polymerization processes find wide applications. The iron-peroxydisulfate induced polymerization is quicker and more efficient than the early use of peroxydisulfate alone. A very large part of the work done in the field of peroxydisulfate concerns its use as a radical generator, often in conjunction with a metal ion to suit the type of polymerization.

There has been a comparatively meager amount of investigation in the field of oxidations of metal and metal complexes by peroxydisulfate in spite of its intense oxidizing power. One of the reasons is that for many of these reducing agents, oxidation by peroxydisulfate does not proceed at a convenient rate around 25° unless a catalyst is present, even though the free energy change is so favorable. At higher temperatures, peroxydisulfate itself undergoes decomposition and introduces serious complications in the system.⁶⁹ Further, the peroxydisulfate oxidations almost always involve the production of the highly reactive sulfate radical ion (exception⁵⁰), which brings about undesirable and unresolvable obstacles to the elucidation of the mechanism of many systems. Kinetics is highly susceptible to influence by traces of foreign matter in the water and to oxygen and so extraordinarily painstaking efforts are needed in some cases to get reproducible and meaningful results. A large number of early published works on this subject reflect such anomalies.^{29,44}

The peroxydisulfate oxidations are very similar to the oxidations by hydrogen peroxide, which involve the $\text{OH}^\cdot$ radical as the intermediate in many of its reactions^{99,100,101}. In both systems, the peroxide bond is symmetrically cleaved and all the complexities that arise from the generation of highly reactive inorganic radicals are common to both of them.

The unfavorable rates of oxidation of many metals and complexes with peroxydisulfate necessitate the use of a catalyst to make them proceed at reasonable rates. One of the most widely used catalysts has been Ag(I) ion.^{56,102} Other metal ions such as Cu(II) , Fe(II) have also been used to some extent. The work in this area has been fairly extensive and has lead to the observation of some simplified and common trends in the diverse systems.^{56,102}

The Ag(I) catalysis of $\text{S}_2\text{O}_8^{2-}$ ion oxidations was first observed by Marshall⁷⁹. Various kinetic investigations show that for a majority of the reducing agents^{16,29,32,44,49,64,65,66,103,104,105} studied, the rate law is given by

$$\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = k_2[\text{S}_2\text{O}_8^{2-}][\text{Ag}^+] \quad (15)$$

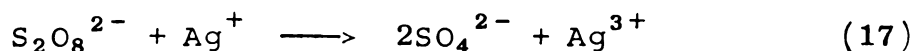
This indicates that the rate of the reaction is proportional to $\text{S}_2\text{O}_8^{2-}$ and Ag(I) ion concentrations, and is independent of the nature and concentration of the reducing agent. The nature of the rate law proves that the rate determining reaction between peroxydisulfate and Ag(I) ion yields one or more intermediates capable of rapidly oxidizing the

reducing agents in these reactions. Further, when positive ions are the reducing agents, the second order rate constants have similar magnitudes and can reasonably be represented as

$$\log k_2 = -.193 - .38_{\mu}^{1/2} \quad 56 \quad (16)$$

The values for the rate constants for uncharged molecules and negatively charged ions are much larger and do not conform to any apparent simple form.

Two different mechanisms have been proposed to explain the Ag(I) ion catalysis of peroxydisulfate oxidations. Yost¹⁰³ proposed the step involving the formation of Ag(III) ion

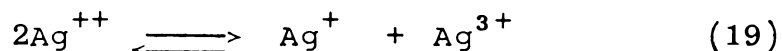


followed by the rapid oxidation by Ag(III). Bawn and Margerison¹⁶ proposed that the rate determining step involves a one-electron oxidation-reduction reaction.



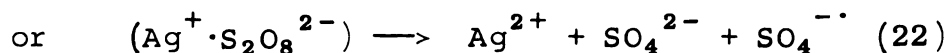
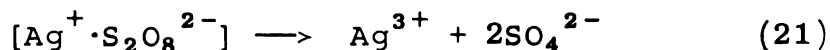
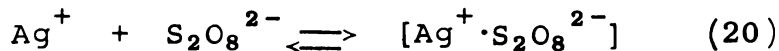
There have been several publications favoring either of them.

According to Wilmarth and Haim¹⁰² the chemical properties of the higher oxidation states of silver are compatible with either of these. In highly acidic media, Ag(II) may be readily prepared and magnetic susceptibility and oxidation potential measurements^{84,85} indicate that the position of the equilibrium in



is far to the left in HNO_3 and HClO_4 at concentrations greater than 4 M. There is evidence that basic Ag(III) salts are produced when Ag(II) solutions are diluted.⁶³ None of the reactions studied identifies the species formed in the rate determining step of the peroxydisulfate and Ag(I) ions, or the reaction intermediates responsible for the oxidation of the reducing agents. Moreover, the reaction intermediates may not be the same in all the cases and in some cases, more than one intermediate may be involved in the oxidation.

Another anomaly in the proposed mechanism is that the entropies of activation of many Ag(I) catalyzed reactions are highly negative, which is in conflict with the value of approximately $+20 \text{ cal}^0\text{K}^{-1}\text{mol}^{-1}$ expected from the proposed rate determining step.⁵⁶ In this connection however, the alternate initial step suggested by Bekier and Kijowski¹⁸ and Chalatykyan and Beilerian²⁷ may be cited.

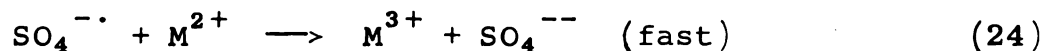
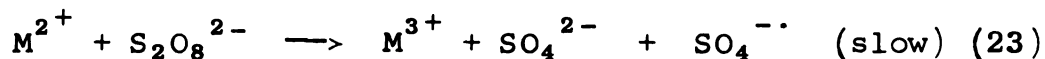


The overall negative entropy can be explained because step 21 or 22 will involve a large negative entropy.⁴⁵ In the present investigation, a similar step has been proposed for the Fe(II) complexes and peroxydisulfate. Although the overall entropy is negative, a positive entropy of about

$15 \text{ Cal}^0 \text{K}^{-1} \text{mol}^{-1}$ has been calculated for the corresponding step 1.

Chain reactions represent another widely investigated area in the chemistry of peroxydisulfate ion. These are mostly in organic systems which are capable of participating in chain initiation and termination steps. This subject will not be dealt with any further in this work.

Very few cases of direct oxidation of metal ions and their complexes by peroxydisulfate have been studied. These include the oxidation of Fe^{2+} ,^{40,68} some tris complexes of $\text{Fe}(\text{II})$ and $\text{Os}(\text{II})$ with bipyridine and phenanthroline derivatives^{25,60,61} and ferrocyanide.^{28,55} The rate determining step was postulated as



A slightly different step has been suggested in this investigation as explained in later chapters.

EXPERIMENTAL

A. Preparation of Reagents:

Reagent grade materials were used throughout. 2,2'-Bi-pyridine, 1,10-phenanthroline and their derivatives were obtained from K. and K. Laboratories Inc. The water used to prepare the solutions was doubly distilled over alkaline potassium permanganate in a Pyrex vessel and stored in stoppered Pyrex flasks. This method was preferred to demineralization by passing through organic resins as the latter might introduce some organic matter as an impurity. The presence of even traces of organic matter has been shown to affect the course of the peroxydisulfate reactions very seriously and leads to irreproducible and erroneous results.

One such illustration is the presence of alcohol, which is discussed later in this work.

The glassware used was thoroughly washed with chromic acid solutions, rinsed with distilled water, conductivity water and then was air dried.

Standard solutions of peroxydisulfate were prepared by weighing exact quantities of the reagent and dissolving them in appropriate quantities of doubly distilled water; the solutions were prepared fresh daily and were never kept for more than 10-12 hours. This precaution prevented the possibility of radical initiation or any other complication that might arise from the decomposition of peroxydisulfate.

The rate of decomposition of the peroxydisulfate under the conditions of the experiment, however, was very slow and the results were reproducible within the limits of experimental errors.

2,2'-Bipyridine, 1,10-phenanthroline and their derivatives were used without further purification. The sulfates of these complexes were prepared by dissolving three equivalents of the organic base in water and adding a freshly prepared aqueous solution containing one equivalent of ferrous sulfate. The complexes were formed instantaneously. The absorptivities were checked spectrophotometrically for the complete formation of the complex.

The complex perchlorates were precipitated from the sulfate solutions with sodium perchlorate, washed thoroughly with water and redissolved. Solutions of sodium sulfate and sodium perchlorate were prepared by dissolving the salts in distilled water.

B. Analytical Methods:

Spectrophotometry was used to determine the initial concentration of the Fe(II) complexes and to follow the course of the reactions. The wavelength of the maximum absorption and the molar absorptivities of the tris Fe(II) and Fe(III) complexes were checked and were found to agree with the values reported earlier.⁴¹ The values of molar absorptivities are given in Table I.

Table I. Molar absorptivities of the substituted 1,10-phenanthroline and 2,2'-bipyridine complexes of iron(II) and iron(III).

Ligand	Wavelength of maximum absorption (mμ)		Molar absorptivity (cm ² mole ⁻¹)	
	Iron(III)	Iron(II)	Iron(III)	Iron(II)
1,10-Phenanthroline	602	510	870	11,100
5-Methyl-1,10-phenanthroline	597	516	770	11,500
5-Nitro-1,10-phenanthroline	590	510	950	11,500
5-Chloro-1,10-phenanthroline	595	512	760	11,700
2,2'-Bipyridine	617	522	320	8,650
4,4'-Dimethyl-2,2'bipyridine	591	529	390	8,470

Solutions of Fe(II) complexes were found to obey Beer's law in the range of concentrations used. The absorptivities of the Fe(III) complexes are very low compared to the Fe(II) complexes and so no correction for their absorption was used except in the later parts of some reactions where it was significant.

In the experiments to check the stoichiometry, spectrophotometry was used to determine the Fe(II) complex concentrations. The peroxydisulfate was determined according to the following method:⁶⁷

Potassium iodide was added to a known volume of peroxydisulfate and the mixture was allowed to stand in the dark for 15-20 min. The iodine liberated was determined by titration with a standard solution of sodium thiosulfate, by use of a freshly prepared solution of starch as indicator. Very good endpoints were obtained.

The same procedure was used to check whether any loss of $K_2S_2O_8$ had occurred during the reaction. The Fe(II) complex and $K_2S_2O_8$ were allowed to react and after the reaction was complete, KI was added. In this case, however, the Fe(III) complex also oxidized the iodide and the total quantity of iodine liberated was determined as before. The total amount of $S_2O_8^{2-}$ before and after the titration were compared.

C. Procedure

Exact volumes of the standard potassium peroxydisulfate (usually 10^{-2} M) and Fe(II) complex solution were placed in the two separate arms of an H-shaped vessel joined together at the top. The amount of Fe(II) was adjusted so that it would be in the concentration range within which Beer's law is obeyed. The volumes of the samples were adjusted to be 10 ml so that the concentration of each of the reactants after mixing was easily calculated. The tubes were stoppered with Pyrex caps or polythene stoppers and were allowed to warm up in a constant temperature water bath to the required temperature. The temperature of the bath was measured with a thermometer graduated in 0.10 degree and the temperature of the bath could be adjusted to within $\pm 0.05^{\circ}$. Water from the bath was circulated by a centrifugal pump through the water jacket of the spectrophotometric cell compartment.

The spectrophotometer cells were washed with conductivity water and after air drying were placed in the thermostated cell compartment. When the cell had attained the bath temperature, the reactants were mixed by inverting the tubes a few times while still being immersed in the bath, and were then quickly transferred to the cells. The time of mixing was taken as the zero time of the reaction. Readings on the spectrophotometer could be started in most cases within 30 seconds of mixing.

To monitor the course of the reactions, a Beckman Model DU spectrophotometer (later an Unicam Model S.P. 800-B spectrophotometer) was used. For most reactions, cells with a 1 cm pathlength were used; however, in a few reactions where concentrated Fe(II) solutions were involved cells with 0.1 cm path length were used. The temperature of the solutions after the reaction was checked and found to be unchanged. Duplicate experiments with the Beckman Model DU and the Unicam spectrophotometers agreed very well. The extent of the reaction was determined from the value of the absorbance at various times.

As the reactions were mostly carried out under pseudo-first order conditions by keeping the $S_2O_8^{2-}$ in large excess with respect to the Fe(II) complexes the pseudo first order rate constants were obtained from the slope of linear portion of the plot of $-\ln(\text{absorbance})$ versus time. The second order rate constants were obtained by dividing the first order constants by twice the concentration of $S_2O_8^{2-}$.

For each set of concentrations, a total of at least four experiments were performed and the average rate constants were used. The reproducibility was excellent for all the complexes except in the case of 5-NO₂- and 5-Cl-phenanthroline complexes. In those cases, the reaction deviated from the first order plot so early in the runs, that reproducibility was difficult and a large number of runs were performed for each concentration.

D. Errors

There are several sources of error in this investigation. Spectrophotometry is limited to a maximum accuracy of about 1% or more depending upon the magnitude of the absorbance reading. Fortunately in this investigation, the absolute value of the initial concentration of the Fe(II) complexes was not needed accurately for most cases, since the reaction was followed under pseudo first order conditions by keeping $\text{S}_2\text{O}_8^{2-}$ in excess. Hence an error in the absorbance readings should introduce a comparatively smaller error in the rate constants determined from the slope of the first order plot.

The most serious source of errors in this investigation is caused by the complicated side reactions discussed in the DISCUSSION section. This is especially true for the oxidation of 5-nitro- and 5-chloro-phenanthroline complexes. Although the measurement of absorbances was started in less than 30-40 seconds after mixing, and the rate constants calculated from the linear portion of the first order plot, the rate constants may be subject to unestimable and perhaps large errors, in view of the deviation from the regular first order plot very early in the reaction.

In the other cases (bipyridine, phenanthroline, dimethylbipyridine, 5-methyl phenanthroline) however, the deviation occurred only after considerable time interval and the reproducibility of the results over a period of about

two years using different reagents, different spectrophotometers and water baths, gives one confidence in the results.

The temperature of the water bath could be controlled to within $\pm 0.05^{\circ}$ and the errors caused by the variations of temperature could be considered negligible.

THEORETICAL

The determination of the rate law for simple reactions involves the use of some direct graphical or mathematical procedures available in many of the standard text books^{4,19,45}. If however, the system under study is more complex and involves opposing, concurrent, consequent reactions or formation of stable intermediates prior to reaction etc., elementary methods of determining the rate law may be impractical or impossible. In such cases, the data are fitted to equations for the various possible rate laws to determine which one is obeyed. Additional information about the reaction in question, such as attainment of equilibrium, concentrations at equilibrium, nature of influence of some added substances (inert or participating in the reaction) etc., can be of great help in narrowing the search for the correct rate law.

In the present investigation, studies were conducted under pseudo first order conditions by keeping a large excess of $S_2O_8^{2-}$ with respect to the Fe(II) complex. The concentration of $S_2O_8^{2-}$ was varied from 1×10^{-3} M to 5×10^{-3} M and that of the complexes was maintained at $5-7 \times 10^{-5}$ M for most of the experiments. A few experiments with higher concentrations of Fe(II) and $S_2O_8^{2-}$ were performed. The data was analyzed as first order rates:

$$-\frac{dFe(II)}{dt} = 2k_2^*[S_2O_8^{2-}][Fe(II)] \quad (25)$$

Since $[S_2O_8^{2-}]$ is essentially constant in each experiment, it can be written as a pseudo first order reaction

$$-\frac{d[Fe(II)]}{dt} = k_2'[Fe(II)] \quad (\text{where } k_2' = 2k_2^*[S_2O_8^{2-}]) \quad (26)$$

and

$$-\ln \frac{[Fe(II)]}{[Fe(II)]_0} = k_2't \quad (27)$$

k_2' is obtained as the slope of the graph of

$-\ln \frac{[Fe(II)]}{[Fe(II)]_0}$ versus time.

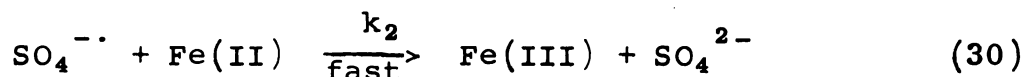
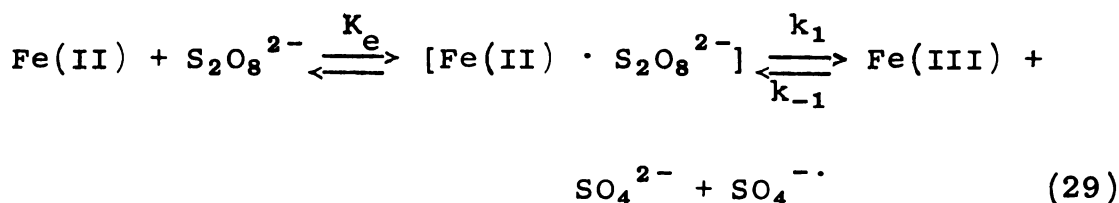
$$k_2^* = \frac{k_2'}{2[S_2O_8^{2-}]} \quad (28)$$

In this study, $-\log$ of the absorptivities of the solution at various times were plotted against time, because the concentration of the $Fe(II)$ complex is proportional to the absorbance.

$[Fe(II)] = \text{absorbance}/\text{Molar absorptivity}.$

k_2^* was evaluated from $\frac{\text{slope} \times 2.303}{2[S_2O_8^{2-}]}$.

The second order rate constants so obtained showed an inverse dependence on the $S_2O_8^{2-}$ concentration and the values could be fitted to a slightly modified form of the second order reaction, in which the formation of a loose complex or ion pair between the $Fe(II)$ and $S_2O_8^{2-}$ ions is assumed to form before the oxidation. The proposed mechanism is:



The reverse step with rate constant k_{-1} is proposed to explain the deviation from the second order conditions, as explained in the DISCUSSION section.

If $k_2 \gg k_{-1}$ and excluding the reverse step for initial stages of the reaction, the reaction rate is

$$-\frac{d\text{Fe(II)}}{dt} = 2k_1[\text{Fe(II)} \cdot \text{S}_2\text{O}_8^{2-}] = 2k_1K_e[\text{Fe(II)}][\text{S}_2\text{O}_8^{2-}] \quad (31)$$

$[\text{S}_2\text{O}_8^{2-}]$ is constant under experimental conditions. Integration gives

$$k_2^* = k_{\text{ob}} = \frac{k_1K_e}{1 + K_e[\text{S}_2\text{O}_8^{2-}]} \quad [\text{Ref. 43}] \quad (32)$$

$$\frac{1}{k_{\text{ob}}} = \frac{1}{k_1K_e} + \frac{K_e[\text{S}_2\text{O}_8^{2-}]}{k_1K_e} \quad (33)$$

k_1K_e is the forward rate constant of the reaction. A plot of $1/k_{\text{ob}}$ versus $[\text{S}_2\text{O}_8^{2-}]$ gives the intercept $= 1/k_f = 1/k_1K_e$ and slope $= K_e/k_f$ from which K_e is calculated.

If the reverse step involving the reaction of $\text{Fe(III)} - \text{SO}_4^{2-}$ ion pair and $\text{SO}_4^{\cdot -}$ is incorporated, the rate law is

$$- \frac{d\text{Fe(II)}}{dt} = k_1 K_e [\text{Fe(II)}] [\text{S}_2\text{O}_8^{2-}] - k_{-1} [\text{Fe(III)} \cdot \text{SO}_4^{2-}] [\text{SO}_4^{\cdot-}] + k_2 [\text{Fe(II)}] [\text{SO}_4^{\cdot-}] \quad (34)$$

If a steady state approximation is assumed,

$$[\text{SO}_4^{\cdot-}]_{ss} = \frac{k_1 K_e [\text{Fe(II)}] [\text{S}_2\text{O}_8^{2-}]}{k_2 [\text{Fe(II)}] + k_{-1} [\text{Fe(III)}]} \quad (35)$$

If $k_{-1} [\text{Fe(III)}] \ll k_2 [\text{Fe(II)}]$,

$$[\text{SO}_4^{\cdot-}]_{ss} = k_1 K_e [\text{S}_2\text{O}_8^{2-}] / k_2 \quad (36)$$

Substituting in (34)

$$\begin{aligned} - \frac{d\text{Fe(II)}}{dt} &= 2k_1 K_e [\text{Fe(II)}] [\text{S}_2\text{O}_8^{2-}] - \frac{k_{-1}}{k_2} (k_1 K_e [\text{S}_2\text{O}_8^{2-}] [\text{Fe(III)}]) \\ &= 2\bar{K} [\text{Fe(II)}]_0 - 2[\bar{K} + k'_{-1}] [\text{Fe(III)}] \end{aligned} \quad (37)$$

where

$$\bar{K} = \frac{k_1 K_e [\text{S}_2\text{O}_8^{2-}]}{1 + K_e [\text{S}_2\text{O}_8^{2-}]}$$

and

$$k'_{-1} = 1/2 \frac{k_{-1}}{k_2} (k_1 K_e) [\text{S}_2\text{O}_8^{2-}], \quad [\text{Fe(II)}]_0 = \text{initial concentration of Fe(II) complex.}$$

At equilibrium,

$$\bar{K} [\text{Fe(II)}]_0 = (\bar{K} + k'_{-1}) [\text{Fe(III)}] \quad (38)$$

Writing

$$\frac{[\text{Fe(III)}]_{eq}}{[\text{Fe(II)}]_0} = f \quad (39)$$

where $[\text{Fe(III)}]_{eq}$ is the concentration of Fe(III) complex at equilibrium,

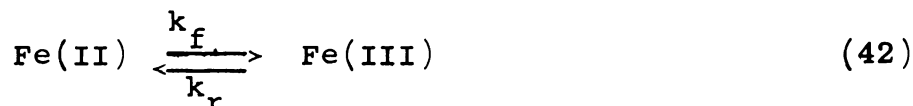
$$k'_{-1} = \bar{K}(\frac{1}{f} - 1) \quad (40)$$

or

$$k_{-1}/k_2 = \frac{2}{1+K_e[S_2O_8^{2-}]} (\frac{1}{f} - 1) \quad (41)$$

Hence if the initial and equilibrium concentrations of Fe(II) are known, k_{-1}/k_2 can be calculated.

k'_{-1} can be graphically determined as follows, if the reaction is considered as a simple first order reversible reaction (since the concentration of $S_2O_8^{2-}$ is essentially constant)



where

$$k_f = 2k_1K_e[S_2O_8^{2-}] \text{ and } k_r = \frac{k_{-1}}{k_2} (k_1K_e)[S_2O_8^{2-}].$$

The rate law for this reaction, if the initial concentration of Fe(III) is zero is:

$$\frac{-\ln \left\{ \frac{[Fe(II)] - [Fe(II)]_{eq}}{[Fe(II)]_0 - [Fe(II)]_{eq}} \right\}}{(k_f + k_r)t} = [Ref. 4] \quad (43)$$

where $[Fe(II)]$, $[Fe(II)]_0$, $[Fe(II)]_{eq}$ are concentrations of the Fe(II) complex at time t , zero time and at equilibrium, respectively. Since k_f is known, k_r can be calculated.

$$\frac{k_{-1}}{k_2} = \frac{2k_r}{k_f} \quad (44)$$

The ratio k_{-1}/k_2 obtained by the two methods can be compared.

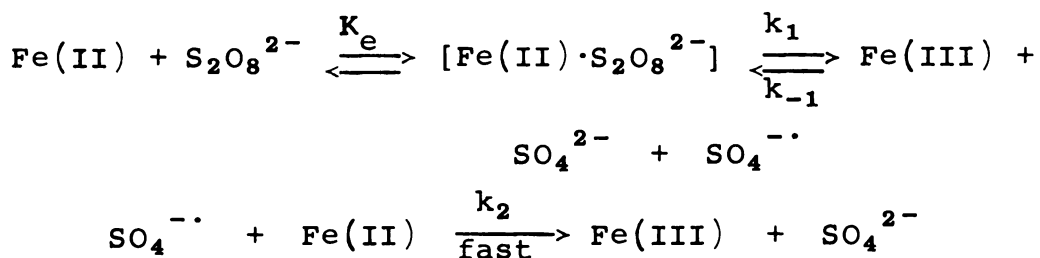
RESULTS

Determination of the Rate Constants

Preliminary studies to check the order of the reaction showed that the rate of the reaction was first order with respect to Fe(II) and the rate constant was invariant with the change in concentration of Fe(II). But when the concentration of Fe(II) complex was kept constant, and the concentration of peroxydisulfate varied, it was found that the second order rate constants showed a decrease with increasing concentrations of peroxydisulfate. See Table II. The pseudo first order constants seemed to level off at high concentrations of peroxydisulfate.

In a few of the initial experiments, the complex perchlorates were used. Later, due to their limited solubility, the perchlorates were replaced by sulfates. The rate constants for the perchlorates studied are given in Table III. They compare well with the values for sulfates, for the same concentrations of peroxydisulfate.

The experimental data could be successfully fitted to the rate law corresponding to the mechanism:



As explained in the THEORETICAL section, the values of the forward rate constants and the equilibrium constants have

Table II. Dependence of the second order rate constants on the concentration of peroxydisulfate.

$[S_2O_8^{2-}] \times 10^3 M$	Second Order Rate Constants ($M^{-1}sec^{-1}$) $\times 10^1$			
	25°	30°	35°	40°
(a) <u>Tris</u> -(2,2'-Bipyridine)-iron(II) sulfate:				
1.0	3.35	4.52	5.49	7.1
1.5	2.90	--	4.78	6.34
2.0	2.69	3.46	4.40	5.5
2.5	2.48	3.34	4.15	5.2
3.0	2.33	3.10	3.74	4.62
3.5	--	3.06	--	--
4.0	2.14	2.75	3.49	4.06
5.0	1.85	2.60	--	--
(b) <u>Tris</u> -(4,4'-Dimethyl-2,2'-bipyridine)-iron(II) sulfate $\times 10^0$				
0.50	4.67	6.02	6.93	8.10
1.0	3.55	5.15	5.56	6.50
1.5	3.07	3.84	4.52	4.95
2.0	2.75	3.23	4.00	--
2.5	--	3.10	--	--
(c) <u>Tris</u> -(1,10-Phenanthroline)-iron(II) sulfate $\times 10^1$				
1.0	1.70	2.30	3.36	4.20
1.5	--	--	3.04	3.36
2.0	1.30	1.92	2.60	3.08
2.5	--	--	2.40	--
3.0	1.23	1.73	2.24	2.61
3.5	--	1.60	--	--
4.0	1.01	1.54	1.92	2.28

Table II. (Cont.)

$[S_2O_8^{2-}] \times 10^3 M$	Second Order Rate Constants ($M^{-1}sec^{-1}$) $\times 10^2$			
	25°	30°	35°	40°
(d) <u>Tris</u> -(5-Methyl-1,10-phenanthroline)-iron(II) sulfate				
1.0	6.83	11.0	12.9	20.0
1.5	--	9.40	11.6	17.5
2.0	5.80	8.40	11.1	13.3
2.5	--	7.40	10.0	12.0
3.0	5.00	6.78	9.45	11.0
4.0	4.30	6.00	8.40	10.5
(e) <u>Tris</u> -(5-chloro-1,10-phenanthroline)-iron(II) sulfate $\times 10^2$				
1.0	9.50	22.1	31.0	51.5
2.0	4.93	9.15	19.5	30.0
3.0	3.60	6.80	12.5	21.1
4.0	2.86	5.10	9.5	17.9
(f) <u>Tris</u> -(5-Nitro-1,10-phenanthroline)-iron(II) sulfate $\times 10^1$				
1.0	1.72	3.98	5.42	9.00
2.0	0.844	2.03	3.12	5.57
3.0	0.603	1.53	2.45	3.76
4.0	0.456	1.10	1.66	3.03

Table III. Rate constants for the complex perchlorates.

Complex	$[S_2O_8^{2-}] \times 10^3 M$	Second order rate constants $(M^{-1}sec^{-1}) \times 10^1$
<u>Tris</u> -(2,2'-Bipyridine)- iron(II) sulfate	0.5	3.55
	1.0	3.34
	2.0	2.71
Tris-(1,10-Phenanthroline)- iron(II) sulfate	1.0	1.86
	2.0	1.54
Tris-(5-Nitro-1,10-phen- anthroline)-iron(II) sulfate	1.0	1.67
	2.0	0.91
Tris-(5-Methyl-1,10-phen- anthroline)-iron(II) sulfate	1.0	0.710
	2.0	0.575

been calculated graphically by plotting the reciprocals of the observed second order rate constants against the concentration of peroxydisulfate. (Figures 1,2,3,4,5,6) Least square analysis was done on all graphs and the best values for slopes and intercepts along with the standard deviations are given in Table IV.

Another important observation in these reactions is the deviation from the first order plots after different intervals of time for the different complexes. The deviation is large in 5-nitro and 5-chlorophenanthroline complexes, starting in a few minutes after the reaction was started. It is less for 5-methyl phenanthroline complex, starts only after about 50% of the reaction for phenanthroline complex and after 80 to 85% of the reaction for the bipyridine complex. There was very little deviation from the rate equation for the dimethyl bipyridine complex. This deviation was also observed by Irvine⁶¹.

In the present work, it is tentatively suggested that a probable reverse step, with rate constant k_{-1} , involving the reaction of $\text{SO}_4^{\cdot -}$ radical and the $\text{Fe(III)} - \text{SO}_4^{2-}$ ion pair, may at least partly explain the deviation from second order rate law. A detailed discussion of other factors that may be important is given in the DISCUSSION section.

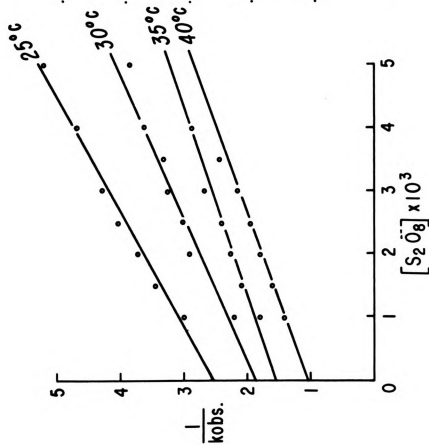
An attempt has been made in the case of phenanthroline and 5-methylphenanthroline complexes to estimate the magnitude of k_{-1}/k_2 by calculation from K_e and concentrations

Figure 1. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(2,2'-Bipyridine)-iron (II) sulfate.

Figure 2. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(4,4'-Dimethyl-2,2'-Bipyridine)-iron(II) sulfate.

I

TRIS-(2,2'-DIPYRIDINE)-
Fe (II) SULFATE



II

TRIS-(4,4'-DIMETHYL-2,2'-DIPYRIDINE)-
Fe (II) SULFATE

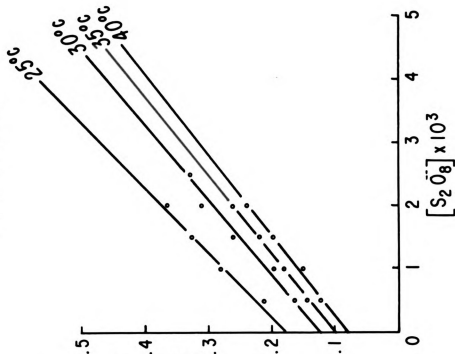
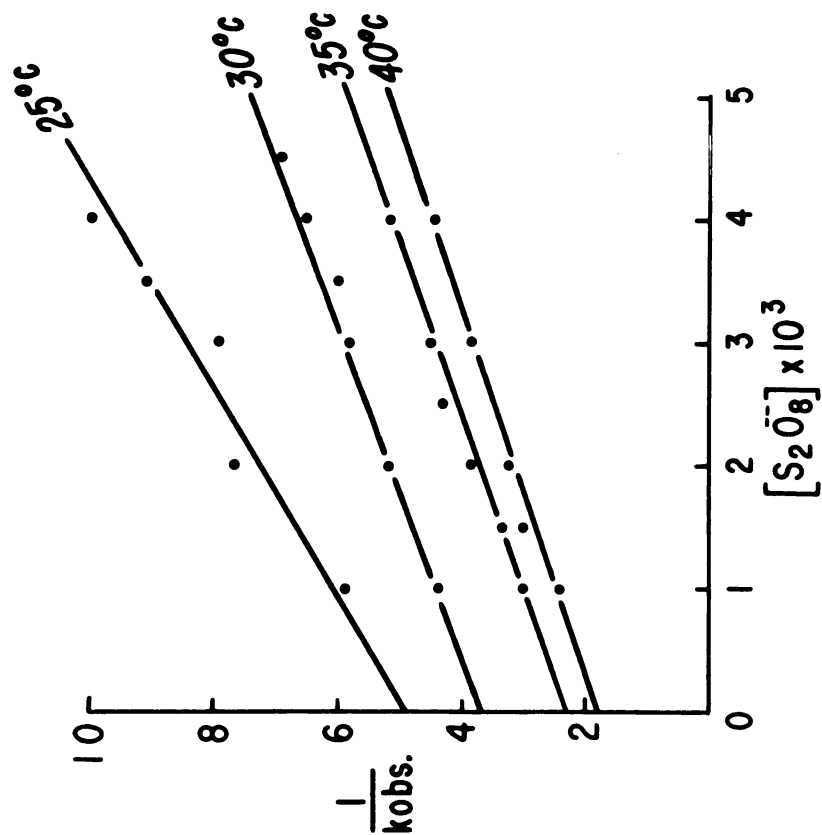


Figure 3. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(1,10-Phenanthroline) - iron (II) sulfate.

Figure 4. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(5-Methyl-1,10-Phenanthroline) - iron (II) sulfate.

III

TRIS-(1,10-PHENANTHROLINE)-
Fe (II) SULFATE



IV

TRIS-(5-METHYL-1,10-PHENANTHROLINE)-
Fe (II) SULFATE

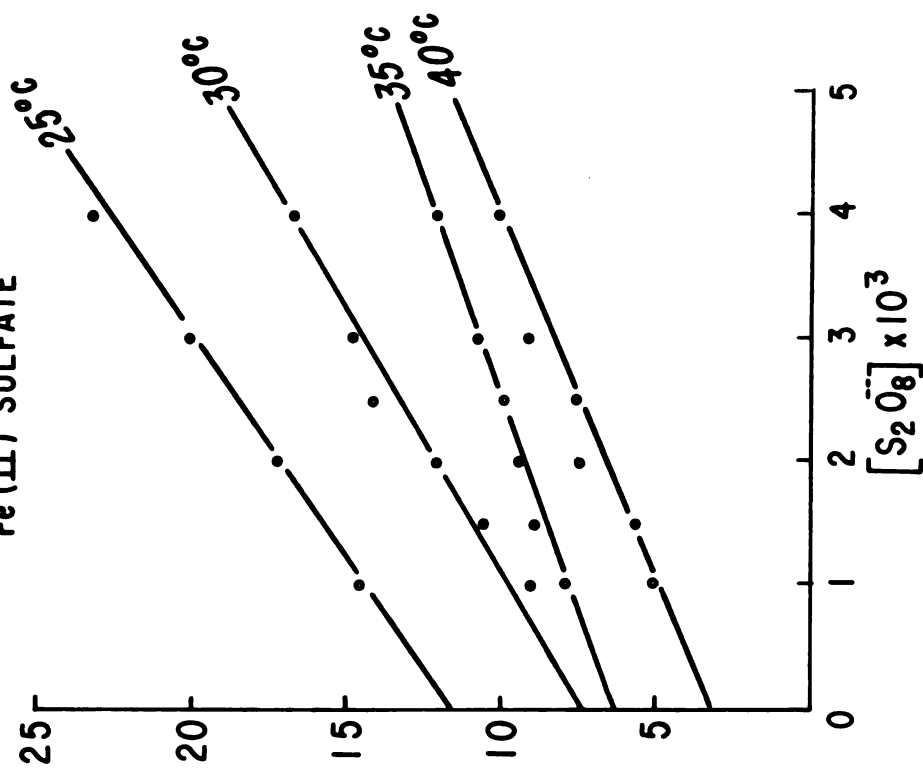


Figure 5. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(5-Nitro-1,10-Phenanthroline) - iron (II) sulfate.

Figure 6. Graph of $1/k_{ob}$. versus peroxydisulfate concentration for tris-(5-Chloro-1,10-Phenanthroline) - iron (II) sulfate.

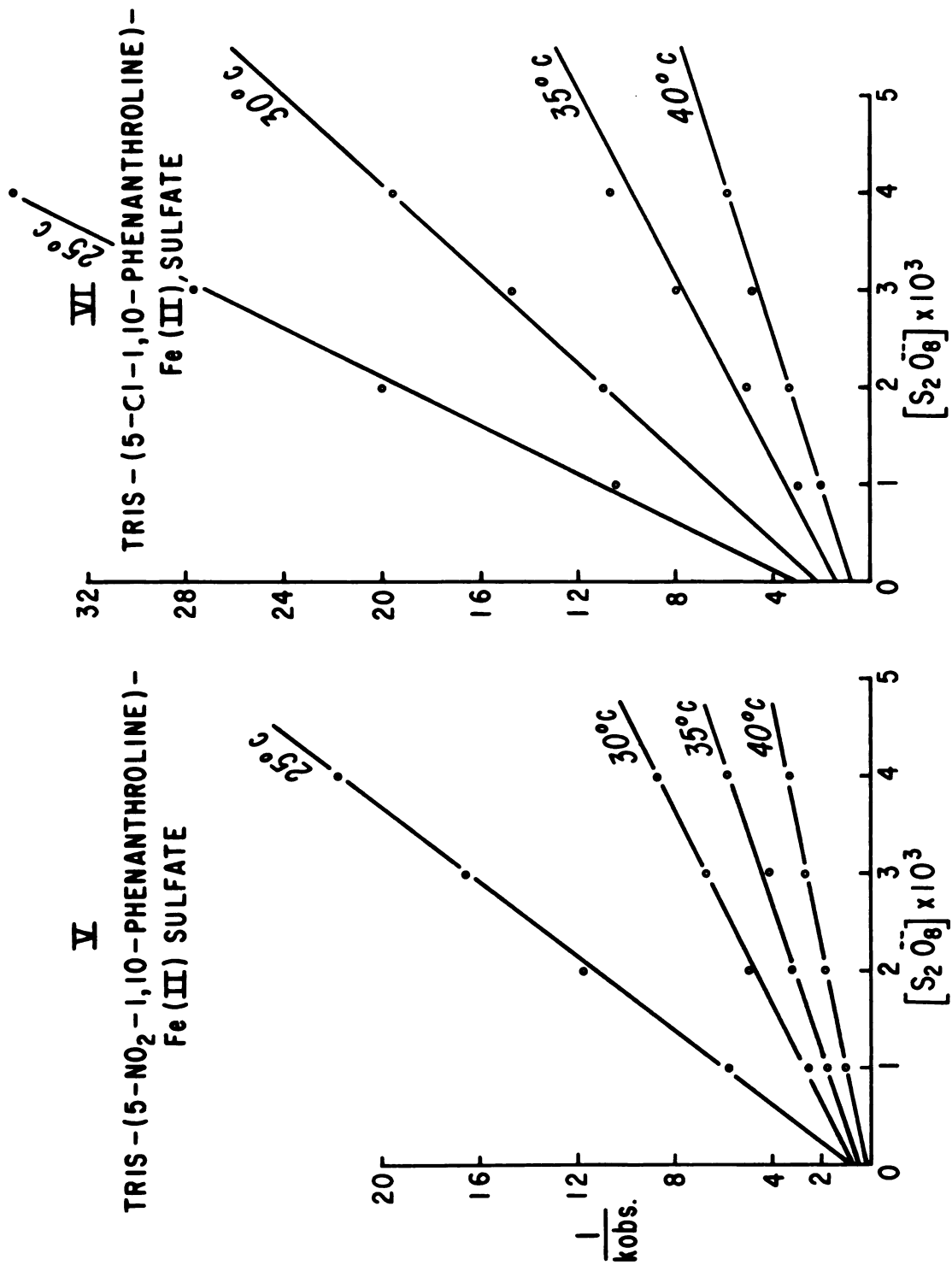


Table IV. Forward rate constants and equilibrium constants

Complex	Temp. °C	$k_f(M^{-1}sec^{-1}) \times 10^1$	$K_e(M^{-1}) \times 10^{-2}$
<u>Tris</u> -(2,2'-Bipyridine)-iron(II) sulfate	25 30 35 40	3.99 ± .17 5.32 ± .03 6.48 ± .2 9.21 ± .10	2.39 ± .12 2.32 ± .24 2.26 ± .32 3.23 ± .10
<u>Tris</u> -(1,10-Phenanthroline)-iron(II) sulfate	25 30 35 40	2.10 ± .2 2.72 ± .12 4.33 ± .17 5.52 ± .12	2.58 ± .46 1.92 ± .21 3.13 ± .19 3.64 ± .29
<u>Tris</u> -(5-Methyl-1,10-phenanthroline)- iron(II) sulfate	25 30 35 40	0.859 ± .13 1.31 ± .21 1.62 ± .15 2.51 ± .38	2.46 ± .12 2.79 ± .22 2.22 ± .35 3.83 ± .66
<u>Tris</u> -(5-Chloro-1,10-phenanthroline)- iron(II) sulfate	25 30 35 40	2.72 ± .20 4.57 ± .24 7.42 ± .40 12.3 ± 3.0	22.6 ± 1.2 23.2 ± 3.1 26.1 ± 5.2 16.0 ± 5.0
<u>Tris</u> -(5-Nitro-1,10-phenanthroline)- iron(II) sulfate	25 30 35 40	12.9 ± 2.1 15.6 ± 2.1 20.7 ± 3.0 28.0 ± 4.0	41.0 ± 1.8 13.5 ± 2.1 27.3 ± 3.2 20.7 ± 3.1
<u>Tris</u> -(4,4'-Dimethyl-2,2'-bipyridine)- iron(II) sulfate	25 30 35 40	57.8 ± 5.0 88.2 ± 5.0 98.6 ± 7.0 123.0 ± 6.0	5.62 ± .30 7.0 ± .48 7.9 ± .60 9.82 ± .70

of reagents, and graphically as explained in the THEORETICAL section. The equilibrium concentration of the iron(II) complex has been estimated by trial and error to give a good linear graph of

$$-\ln \{[\text{Fe (II)}] - [\text{Fe (II)}]_{\text{eq}}\} / \{[\text{Fe (II)}]_0 - [\text{Fe (II)}]_{\text{eq}}\} \text{ versus } t,$$

(see Figure 7). The linearity of such graphs is satisfactory and there is a fair agreement between the directly calculated and graphically determined values of the ratio k_{-1}/k_2 . (Table V).

A few experiments were performed under conditions of excess tris (2,2'-bipyridine)-iron(II) sulfate. These reactions seemed to reach an apparent equilibrium, with less than two equivalents of the Fe(II) complex oxidized for each mole of $\text{S}_2\text{O}_8^{2-}$ present. The second order forward rate constants, calculated from the early stages of these reactions are given in Table VI.

A. Effect of Alcohol on the Reaction

In the earlier stages of this investigation, difficulties arose on account of the insufficient solubilities of the perchlorates of 5-methyl, 5,6-dimethylphenanthroline complexes etc. in water. Hence the use of an ethyl alcohol-water mixture of uniform composition was contemplated, as in the work of Sutin and Fordsmith⁴¹. It was soon realized that alcohol was not just providing a suitable medium in terms of better solubility. A serious retardation by alcohol

Figure 7. Probable occurrence of the Reverse reaction.
Graph of $-\{[\text{Fe(II)}]_t - [\text{Fe(II)}]_{\text{eq}}\}$
versus time for tris-(1,10-Phenanthroline)-
iron (II) sulfate.

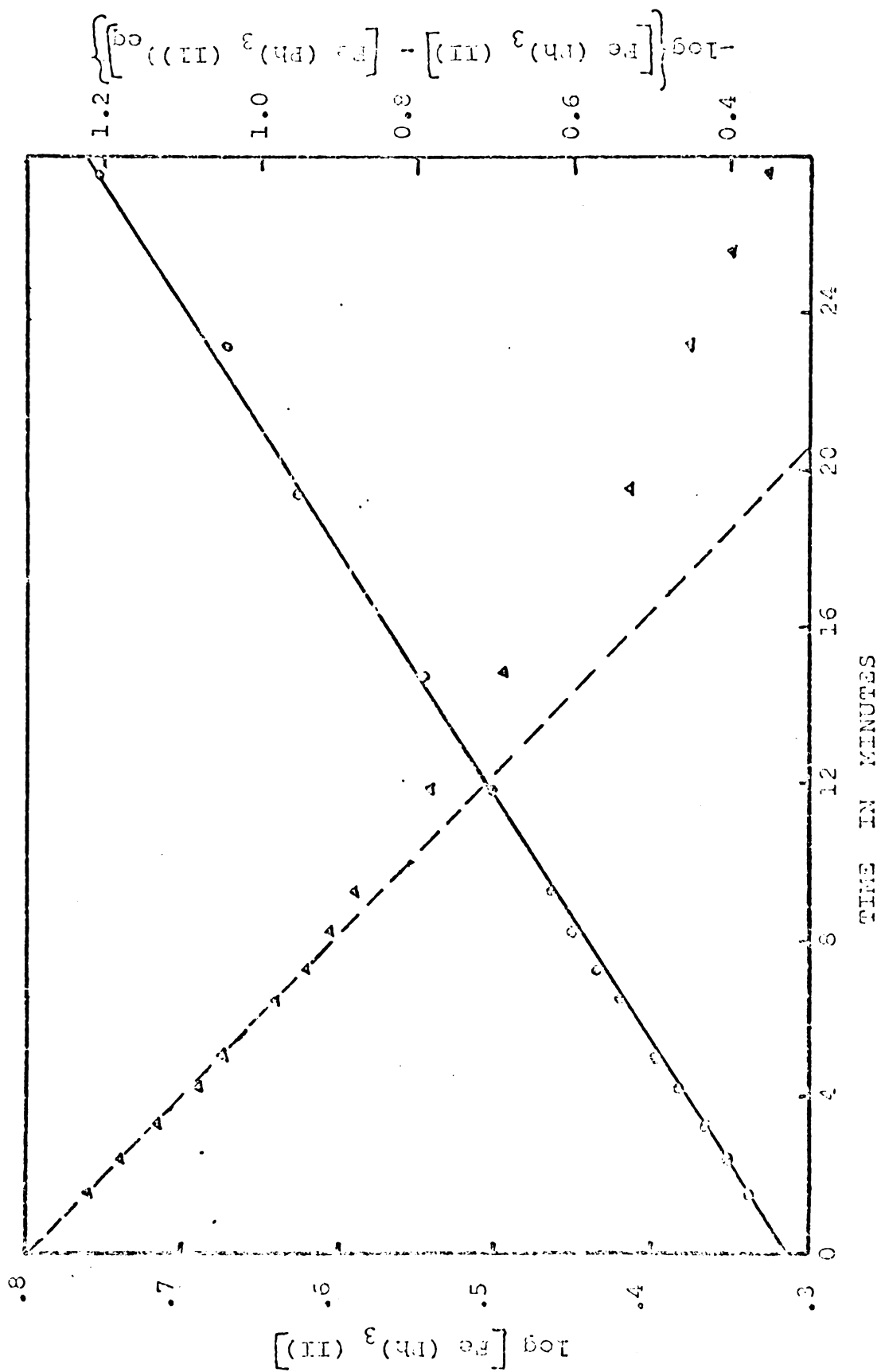


Table V. Values of the ratio k_{-1}/k_2 .

Complex	Temp. °C	$[S_2O_8^{2-}]$ $\times 10^3 M$	$(k_{-1}/k_2) \times 10^1$	
			Direct Calculation	Graphical
<u>Tris</u> -(1,10-Phenanthroline)- iron(II) sulfate	25	1.0	3.2	4.0
		1.5	2.0	1.6
		2.5	1.2	2.5
	35	1.0	5.2	5.1
		1.5	4.0	4.4
		2.0	3.3	3.0
<u>Tris</u> -(5-Methyl-1,10-phenanthroline)-iron(II) sulfate	35	2.5	6.2	5.1
		3.0	5.2	4.9
		3.5	5.0	4.8

Table VI. Rates of reaction, in the presence of excess tris-(2,2'-bipyridine)-iron(II) sulfate. (25°)

Initial Concentrations ($M \times 10^4$)		Second Order Rate Constant ($M^{-1}sec^{-1} \times 10^1$)
$[S_2O_8^{2-}]$	$[Fe(II)]$	
2.0	10.25	2.2
4.0	10.1	2.3

even when present in amounts comparable to $[\text{Fe(II)}]$ and $[\text{S}_2\text{O}_8^{2-}]$ suggested its chemical interaction in the course of the reaction (see Table VII). A systematic study of the reaction by use of a wide range of alcohol concentrations not only clarified the nature of interactions of alcohol but also provided conclusive evidence for the suggested rate determining step of the reaction which had only been a conjecture in earlier work.⁶¹

B. Effect of Sulfate Ions

The effect of sulfate ions in the region $\mu = 0.1$ to 0.4 M was studied for all the complexes. The sulfate ion concentration was varied by varying the amount of sodium sulfate added. The concentration of the complex was maintained at $5-7 \times 10^{-5} \text{ M}$ and that of the peroxydisulfate ion at $5 \times 10^{-3} \text{ M}$. As seen from Table VIII, the rate constants showed very small decrease in this region contrary to the result at lower ionic strength. This phenomenon of little dependence on ionic strength when sulfate ions are in large excess can be explained on the basis of the possible formation of ion pairs between the Fe(II) complex and sulfate ions, which may be the principal species undergoing oxidation at high concentrations of sulfate ions. Such species should react more slowly than free ions and show no dependence on the ionic strength.

An approximate value for the association constant of tris(bipyridine)-iron (II) and sulfate ion is determined by

Table VII. Effect of alcohol concentration on the rate of the reaction. (Temp. 25°)

Initial Concentrations (M).

$[\text{Fe}(\text{DiPy})_3\text{SO}_4]$ $\times 10^5$	$[\text{S}_2\text{O}_8^{2-}]$ $\times 10^3$	$[\text{C}_2\text{H}_5\text{OH}]$	$k_2 (\text{M}^{-1}\text{sec}^{-1})$ $\times 10^2$
6.9	5.0	11.9	1.3
8.1	5.0	8.5	1.2
7.9	5.0	3.4	1.1
6.9	5.0	1.7	1.2
7.5	5.0	0.65	1.2
6.9	5.0	0.17	2.3
7.9	5.0	0.017	11.5
7.9	5.0	0.0017	19.2
7.7	5.0	0.0	21.0

Table VIII. Effect of sulfate ion concentrations on the rates.

Complex	Initial Concentrations (M)			Second order Rate const- and ($M^{-1}sec^{-1}$) $\times 10^1$
	$[S_2O_8^{2-}]$ $\times 10^3$	$[SO_4^{2-}]$ $\times 10^2$	$\mu \times 10^1$	
<u>Tris</u> -(2,2'-Bipyridine)- iron(II) sulfate	1.0	0.1	0.06	2.78
	0.5	0.45	0.15	2.20
	1.0	0.4	0.15	2.19
	2.0	0.3	0.15	2.07
	4.0	0.1	0.15	1.85
	5.0	0.1	0.18	1.85
	5.0	0.2	0.21	1.75
	5.0	0.5	0.30	1.58
	5.0	1.0	0.45	1.43
	5.0	2.0	0.75	1.20
	5.0	2.8	1.0	0.84
	5.0	6.2	2.0	0.84
	5.0	9.5	3.0	0.81
	5.0	12.0	3.75	0.88
<u>Tris</u> -(1,10-Phenanthro- line)-iron(II) sulfate	5.0	2.8	1.0	0.23
	5.0	6.2	2.0	0.22
	5.0	9.5	3.0	0.20
	5.0	12.8	4.0	0.20
<u>Tris</u> -(5-Chloro-1,10- phenanthroline)- iron(II) sulfate	5.0	2.8	1.0	0.19
	5.0	6.2	2.0	0.19
	5.0	9.5	3.0	0.22
	5.0	12.8	4.0	0.18
<u>Tris</u> -(4,4'-Dimethyl-2,2'- bipyridine)-iron(II) sulfate	5.0	2.8	1.0	16.4
	5.0	6.2	2.0	14.0
	5.0	9.5	3.0	12.0
	5.0	12.8	4.0	11.6

plotting -- k_{obs} versus the concentration of sulfate ions (Figure 8). The concentration of $S_2O_8^{2-}$ was maintained at $5 \times 10^{-3} \underline{M}$ and that of SO_4^{2-} varied from $0-1 \times 10^{-2} \underline{M}$. The slope of this graph is $k_a K_a$, from the relationship

$$k_{ob} = k_0 + k_a K_a [SO_4^{2-}] \quad [\text{Ref. 99}] \quad (45)$$

where k_{ob} is the observed rate constant, k_0 and k_a are the rate constants for the free and associated $Fe(II)$ species and K_a = association constant. Assuming $k_a = 8.4 \times 10^{-2} \underline{M}^{-1} \text{sec}^{-1}$ which is the average limiting value in the presence of excess of sulfate ions, the value of $K_a = 6.1 \times 10^1 \underline{M}^{-1}$. The intercept agrees well with the experimentally obtained value for k_0 at $S_2O_8^{2-}$ concentration equal to $5 \times 10^{-3} \underline{M}$.

C. Activation Parameters

The activation energy for the forward rate constants was obtained in the usual way from the relationship

$$\ln k_r = - \frac{E_a}{RT} + \text{constant} \quad (\text{see Figure 9}). \quad (46)$$

From this the enthalpy of activation, entropy of activation and the free energy of activation were calculated from the transition state equation:

$$k_r = \frac{kT}{h} e^{-\Delta G^*/RT} = \frac{kT}{h} e^{(\Delta S^*/R - \Delta H^*/RT)} \quad (47)$$

where

Figure 8. Effect of sulfate ion concentration
on the rate for tris-(2,2'-Bipyridine)-
iron (II) sulfate.

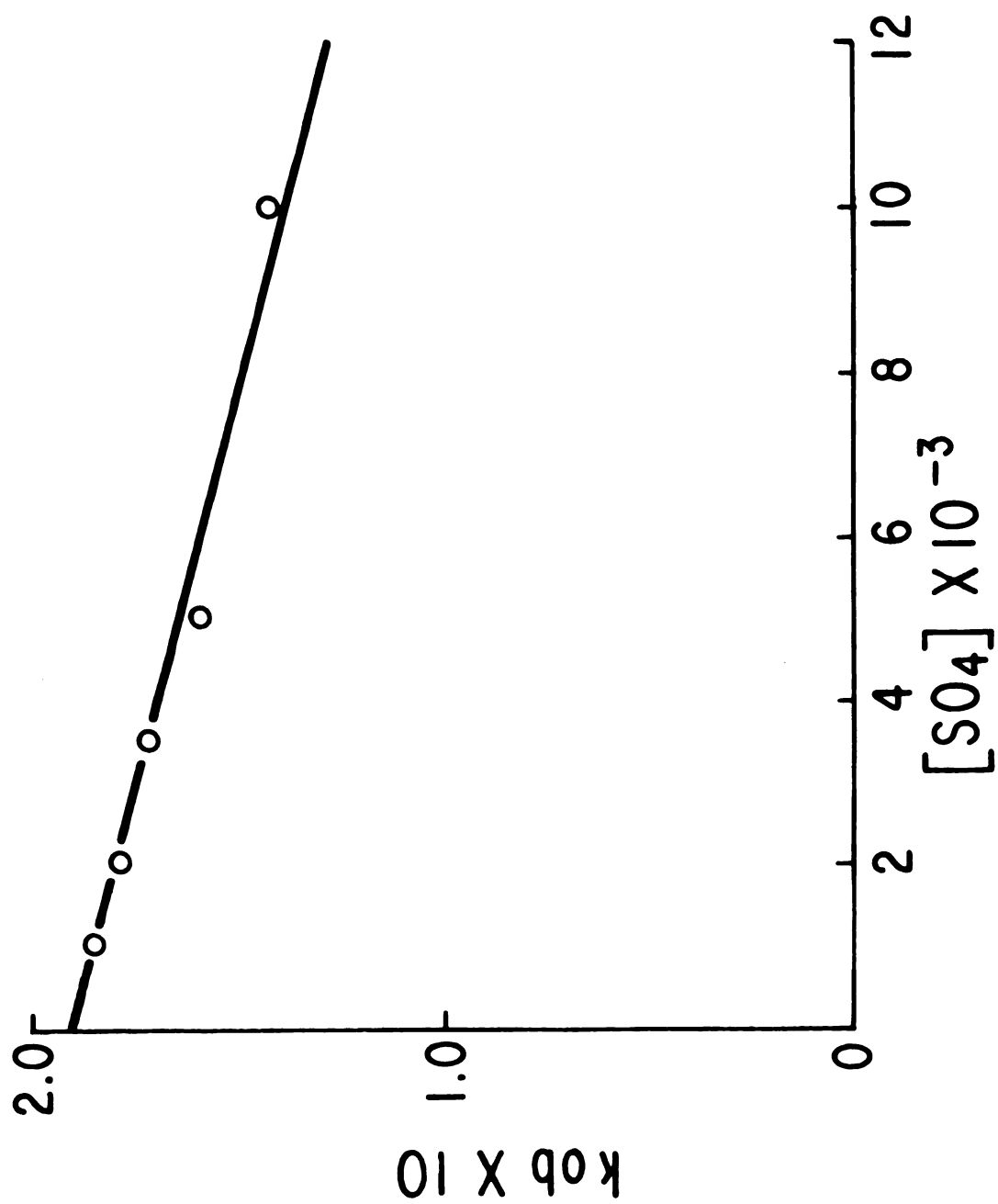
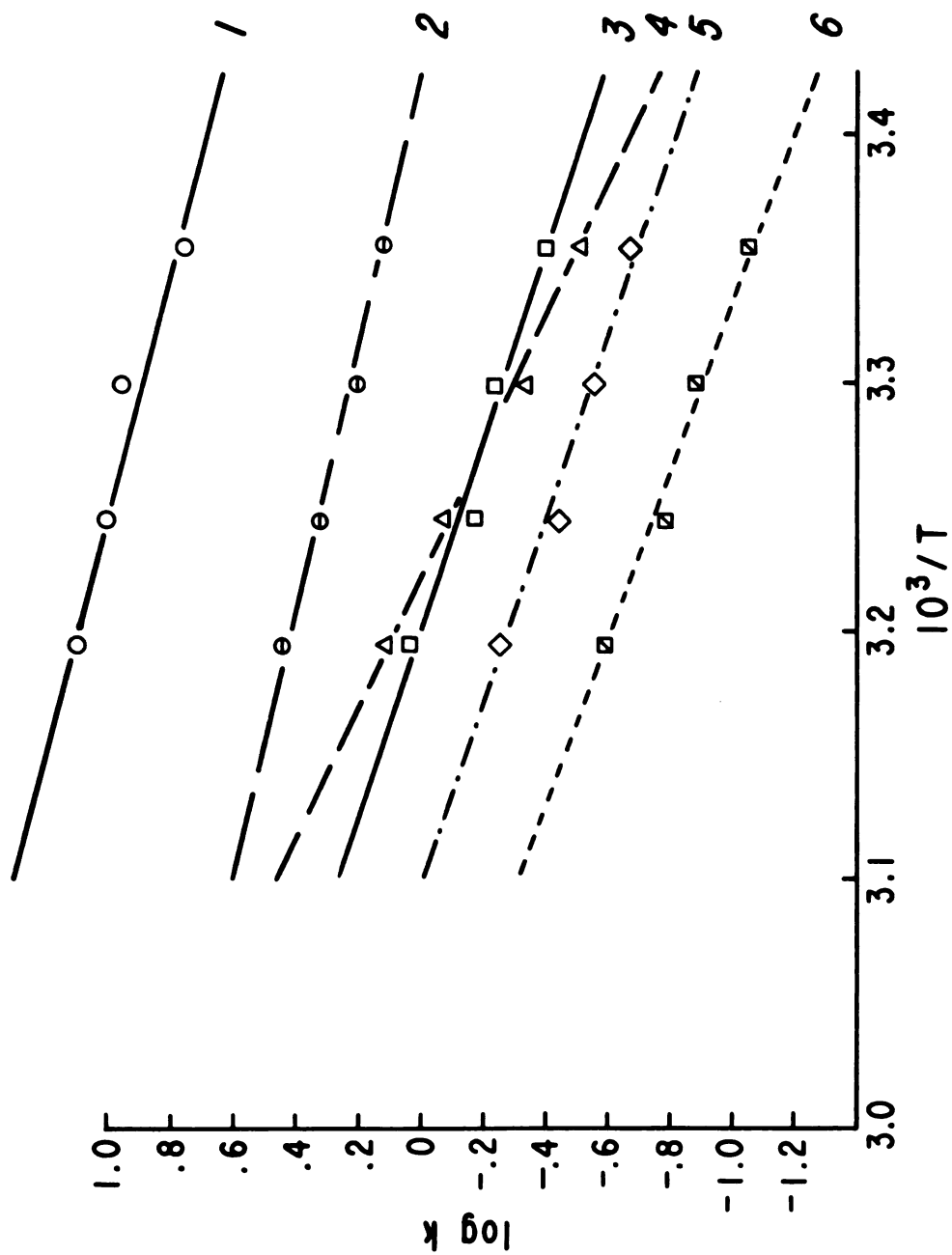


Figure 9. Arrhenius Plot.

Graph of $\log k_f$ versus $1/T$.

1. Tris-(4,4'-Dimethyl-2,2'-Bipyridine)-iron (II) sulfate.
2. Tris-(5-Nitro-1,10-Phenanthroline) - iron(II) sulfate.
3. Tris- (2,2'-Bipyridine)-iron (II) sulfate.
4. Tris-(5-Chloro-1,10-Phenanthroline)-iron (II) sulfate.
5. Tris-(1,10-Phenanthroline) - iron (II) sulfate.
6. Tris-(5-Methyl-1,10-Phenanthroline) - iron (II) sulfate.

ARRHENIUS PLOT



k = Boltzmann's constant,

S^* = entropy of activation per mole,

h = Planck's constant,

T = absolute temperature

H^* = enthalpy of activation per mole,

R = gas constant,

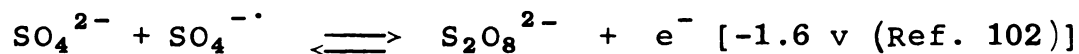
$H = E_a - RT$ (for reactions in solution),

$G^* = H^* - TS^*$.

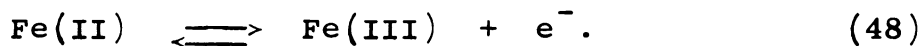
The results are shown in Table IX.

D. Relationship between ΔG^* and ΔG^0

The plot of ΔG^* versus ΔG^0 of the oxidation-reduction step is shown in Figure 10. ΔG^0 is computed by combining the oxidation potentials of the couples;



and



(The oxidation potentials of the corresponding complexes are used.)

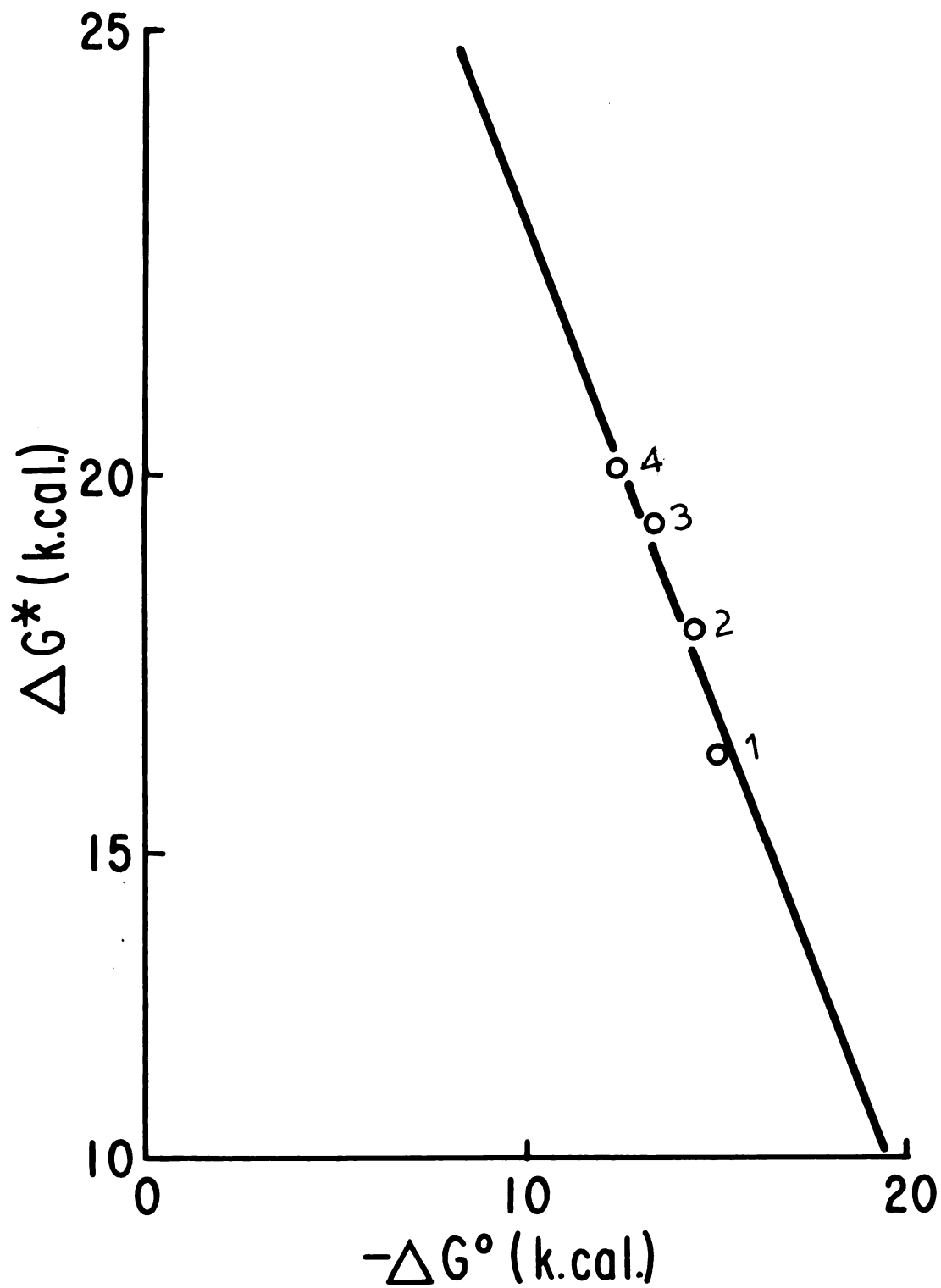
A fairly good linearity is observed for all except 5-nitro- and 5-chlorophenanthroline complexes. The failure of some of these points to lie on the line may be due to experimental errors, as the reproducibility of the rate constants for these complexes was poor, or it may be due to some other factors arising from the negative substituents. The slope of this line is 1.4. This value is in agreement

Table IX. Activation parameters.

Complex	ΔH^* kcal/mole	ΔS^* $\text{cal}^\circ\text{K}^{-1}\text{mol}^{-1}$	ΔG^* kcal/mole
<u>Tris</u> -(2,2'-Bipyridine)- iron(II) sulfate	10.0 ± 1.6	-26.7	18.0 ± 1.6
<u>Tris</u> -(4,4'-Dimethyl- 2,2'-bipyridine)- iron(II) sulfate	7.64 ± 1.74	-29.2	16.3 ± 1.74
<u>Tris</u> -(1,10-Phenan- throline)-iron(II)	12.1 ± 1.67	-21.5	20.0 ± 1.67
<u>Tris</u> -(5-Methyl-1,10- phenanthroline)- iron(II) sulfate	12.2 ± 1.66	-24.7	19.6 ± 1.66
<u>Tris</u> -(5-Chloro-1,10- phenanthroline)- iron(II) sulfate	17.3 ± 2.10	- 7.4	19.5 ± 2.1
<u>Tris</u> -(5-Nitro-1,10- phenanthroline)- iron(II) sulfate	9.10 ± 2.1	-27.6	17.3 ± 2.1

Figure 10. Relation between the free energy of activation and the standard free energy change of the oxidation-reduction step.

1. Tris-(4,4'-Dimethyl-2,2'-Bipyridine)-iron (II) sulfate.
2. Tris-(2,2'-Bipyridine)-iron (II) sulfate.
3. Tris-(5-Methyl-1,10-Phenanthroline) - iron (II) sulfate.
4. Tris-(1,10-Phenanthroline) - iron (II) sulfate.



with the slope of Irvine's graph⁶¹ of $\log k$ versus the overall oxidation potential change. As explained in the DISCUSSION section, not much importance can be attached to the value of this slope.

E. Relationship between the Rate Constants and the pK_a s of the Monoprotonated Ligands and the Hammett Substituent Constants σ

The graph of $\log k$ versus pK_a of the ligands⁴¹ is given in Figure 11. A reasonably linear relationship is obtained at all temperatures studied. Similar straight line relationships are also obtained for the graph of $\log k$ versus σ , the substituent constants⁸⁰ of the Hammett equation⁶², suggesting that substituents do influence the rates of oxidation of the Fe(II) complexes (Figure 12). Such effects have also been observed by other workers.^{21, 41}

F. Errors

The results of the present investigation are subject to the usual experimental errors arising from the limitations of the various methods used. Apart from these, the reactions studied are potentially susceptible to a large number of other complicating factors resulting from the sensitivity of the complexes and the organic ligands to, hydrolysis and oxidation respectively, in the slow reactions. These are discussed in the DISCUSSION section. The formation of the highly reactive $SO_4^{\cdot -}$ radicals is another source of

Figure 11. Relation between the forward rate constants and the pK_a s of the ligands.

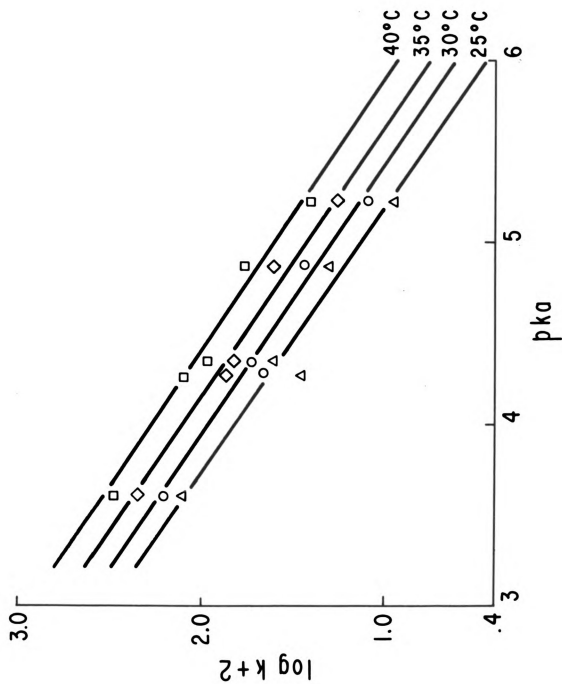
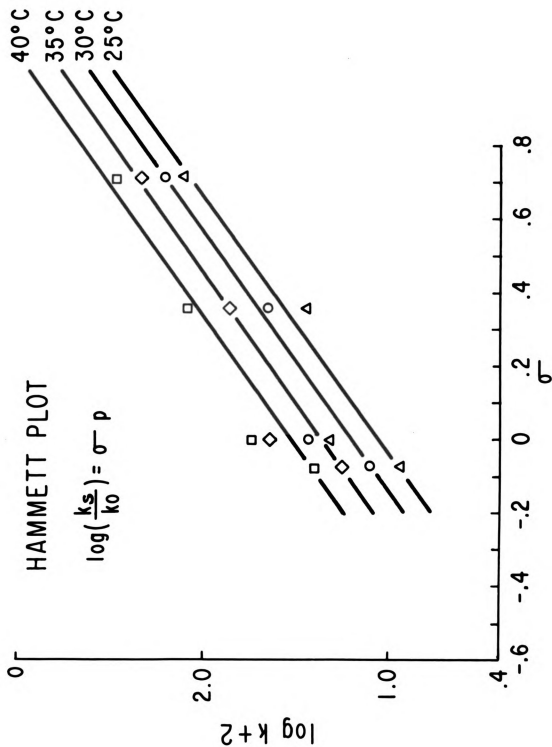


Figure 12. Relation between the forward rate constants and the Hammett substituent constants (ρ) of the ligands.



complication especially in the presence of organic ligands. Added to these is the probable reverse reaction. In view of these difficulties, it is difficult to assess the extent of accuracy, although the reproducibility of the results was good for all except 5-nitro- and 5-chloro-complexes.

DISCUSSION

A. Mechanism

In addition to the reasonably good fit to the rate law of the proposed mechanism for the reaction of the tris complexes of Fe(II) with the substituted 2,2'-bipyridines and 1,10-phenanthrolines, the factors which could be responsible for the decrease in the rate constant with increasing peroxydisulfate concentrations, were considered as follows; the decomposition of the peroxydisulfate itself under the conditions of the experiment is slow⁶⁹ and could not be responsible for the lowering of the rate constants. No oxygen evolution was observed. Moreover, the concentration of the peroxydisulfate ion in all these experiments is much greater than the iron concentration and so a slight undetectable decomposition of peroxydisulfate ion should not alter the rate constants greatly. Another possibility is that the sulfate radical formed in the rate determining step could be involved in the oxidation of the ligand or impurities. Such side reactions have been anticipated or reported by some of the earlier workers^{60,61,10} Irvine⁶⁰ reported that in the oxidation of tris(bipyridine)-osmium(II) with peroxydisulfate ion, only about 1.5 moles of the Os(II) complex were oxidized for each mole of peroxydisulfate ion. He ascribed it to the competition of the metal chelate ions and reducing impurities for the sulfate radical ion formed

in the rate determining step. He could, however, recover all the Os(II)-bipyridine complex by reduction, thus proving the absence of oxidation of the ligand.

Barb and Baxendale¹⁰ reported a considerable oxidation of bipyridine if it is present during catalytic decomposition of H_2O_2 by Fe(III) ion. The conditions of their experiments and the concentrations were much more drastic than in the present investigations.

In the present investigation, absence of extensive ligand oxidation and the oxidation of nearly two moles of the Fe(II) complex for each mole of $\text{S}_2\text{O}_8^{2-}$, were verified as follows for the tris(bipyridine)- and tris(dimethyl bipyridine)-iron(II) complexes; the iron(II) complexes were recovered after the reaction by reduction. Solutions of the tris(bipyridine)-iron(II) complex, were oxidized with a known excess of peroxydisulfate and the total peroxydisulfate plus iron(III) was determined iodometrically after the reaction.⁶⁷ The quantities of sodium thiosulfate needed after the reaction were nearly the same as those required for the blanks, containing the same concentrations of $\text{S}_2\text{O}_8^{2-}$, used initially in the reactions. This suggested the oxidation of two moles of Fe(II) complex for each mole of $\text{S}_2\text{O}_8^{2-}$, because iodine equivalent to the original peroxydisulfate could be formed after the reactions, only if the peroxydisulfate was used up in the oxidation of Fe(II) to Fe(III) . Fe(III) formed could liberate iodine, corresponding to the amount of $\text{S}_2\text{O}_8^{2-}$ used in the oxidation. There

was, however, considerable difficulty in detecting the end point in these titrations when excess Fe(II) complex was used, due to the intense color of the complex.

Irvine⁶¹ calculated the value of k_0 by assuming an ionic strength dependence for k_2 by plotting $\log k_2$ versus $\sqrt{\mu}$ (in the region $\mu = 2.5 \times 10^{-3}$ to 10^{-2} M) and extrapolating it to zero ionic strength. He obtained slopes ranging from -2.5 in the case of tris(2,2'-bipyridine)-ruthenium(II) to -4.4 for tris(dimethylbipyridine)-iron(II) complex. In the present investigation, slopes of -3 to -6 were obtained in this ionic strength region when $K_2S_2O_8$ was used. When the ionic strength was varied by varying the sulfate ion concentration, the plot of $\log k_2$ versus $\sqrt{\mu}$, gave a slope of about -2 at lower concentrations of sulfate ion and practically a zero slope from $\mu = 0.1$ to 0.4 M. Further the rate constants showed a dependence on the peroxydisulfate concentration and could be explained better on the basis of the formation of ion pairs between Fe(II) and sulfate ions. There is justification for assuming the existence of ion pairs because earlier workers have also postulated similar effects. Wells and Salam^{99,100} observed ion pairs of Fe^{2+} and SO_4^{2-} in the oxidation with H_2O_2 and Irvine⁶⁰ in the oxidation of tris(bipyridine)-osmium(II) with peroxydisulfate. Other complexes such as hexammine cobalt(III) and tris(ethylenediamine)-cobalt(III) are also shown to form ion pairs with sulfate ion.⁴⁷ Ion pairs are shown to be important in the oxidation of $Fe(CN)_6^{4-28}$ and I^- by $S_2O_8^{2-}$.⁸⁶

The formation of an intermediate between the iron(II) complex and $S_2O_8^{2-}$ ion is supported by the evidence which follows: Intermediates such as $[M^{n+} \cdot S_2O_8^{2-}]$ have been confirmed in the catalytic oxidation of iodide by peroxydisulfate in the presence of metal ions.⁴⁰ Such an intermediate has been postulated for the oxidation of copper(I) by peroxydisulfate and in the catalytic oxidation of some compounds by peroxydisulfate in the presence of silver ions.^{17,27} A stable diamagnetic intermediate has been observed in the iron(II) iodide-peroxydisulfate system.²⁰

The deviation from the second order rate law after different time intervals for the different complexes was attributed by Irvine⁶¹ to the possible hydrolysis of Fe(II) and Fe(III) complexes. Another possibility is the participation of species other than the complexes of the Fe(II) species in the oxidation. Fordham and Williams⁴⁰ concluded from the bipyridine concentration dependence of the rates in the reaction between peroxydisulfate and an equilibrium mixture of Fe(II) and bipyridine that the reacting species is the bis(bipyridine)-iron(II) complex. They studied the reaction at pH 3.9, a value sufficiently low for the equilibrium between the mono, bis, and tris species to be rapidly established.

In the present investigation, oxidation of the ligand and deviation from the expected stoichiometry seem to be small. Hydrolysis is slow under the present conditions, and further according to Fordham and Williams'⁴⁰ conclusions,

the rate of the reaction for the oxidation of the bis species is very much greater than for the tris species. Hence the hydrolysis of the tris complexes to form a bis species should show an increase in the rate of the reaction rather than the observed decrease. Moreover, the rates of hydrolysis of the tris(bipyridine) and tris(dimethylbipyridine)-iron(II) complexes are greater than that of the phenanthroline complexes, and yet these two fit the rate law better than some others.

The tentative suggestion of a possible reverse step to explain, at least partly, the deviation from the second order rate law was based on Uri's work on the ferrous ion-hydrogen peroxide system.⁹⁶ In an extensive review on inorganic free radicals in solution he gives a critical discussion on the Haber-Weiss mechanism of the catalytic decomposition of H_2O_2 in the presence of Fe^{3+} and its revisions by a number of authors^{8,9,90,98} to give a rate law of the form

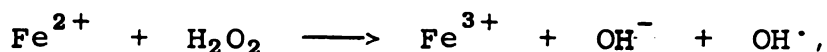
$$\frac{-d(\text{H}_2\text{O}_2)}{dt} = 2k[\text{Fe}^{2+}]_{ss}[\text{H}_2\text{O}_2]$$

where $[\text{Fe}^{2+}]_{ss}$ = steady state concentration of Fe^{2+} . Uri suggests an additional important step not taken into account by earlier workers, namely the reaction:



This is the back reaction of the primary step of the Haber-Weiss mechanism. In the original Haber-Weiss mechanism, the

radical initiation step was represented as:

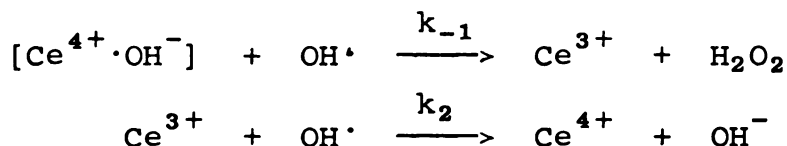


according to which, a reverse step would be highly unlikely due to the necessity of termolecular collisions. Uri considers the ion pair formation necessary and hence a reverse step to the radical initiation step is possible and important. This step is also exothermic to the extent of 5 - 10 kcals.⁹⁶ The rate equation obtained for the catalytic decomposition of H_2O_2 by Fe^{3+} is revised to include the reverse step as

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = 2k_1[\text{Fe}^{2+}]_{ss}[\text{H}_2\text{O}_2] - 2k_{-1}[\text{Fe}^{3+}\cdot\text{OH}^-][\text{OH}\cdot]_{ss}$$

where $[\text{Fe}^{2+}]_{ss}$, and $[\text{OH}\cdot]_{ss}$ denote steady state concentrations. He could thus successfully fit Anderson's data⁶ to the above rate law. Anderson had been unable to explain his data adequately.

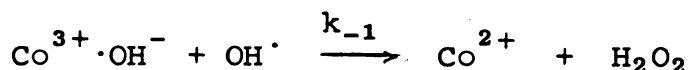
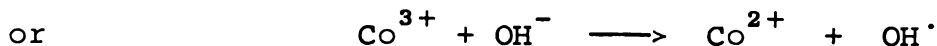
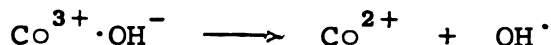
Similar steps have also been proposed for the photo-oxidation of water by Ce(IV) ion by Evans and Uri^{38,39}



and the ratio of k_2 to k_{-1} is calculated to be ~ 10 .

In the reaction of Co(III) ions with water, the rate of the reaction is second order with respect to Co(III) at high Co(III) concentrations and tends to a first order at low concentrations of the latter^{13,14,15} Uri⁹⁶ has proposed

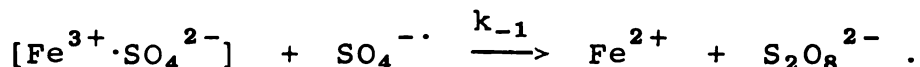
the steps



to explain the change in order, with change in Co(III) concentrations and considers $\text{Co}^{2+} + \text{OH}^\cdot \xrightarrow{k_2} \text{Co}^{3+} + \text{OH}^-$ could become significant only at high concentrations of Co^{2+} ions.

The rate of the two reactions $\text{M}^{n+} + \text{OH}^\cdot \xrightarrow{k_2} \text{M}^{(n+1)+} + \text{OH}^-$ and $[\text{M}^{(n+1)+} \cdot \text{OH}^-] + \text{OH}^\cdot \xrightarrow{k_{-1}} \text{M}^{n+} + \text{H}_2\text{O}_2$, in all these cases depends on the oxidation potential of $\text{M}^{n+} \longrightarrow \text{M}^{(n+1)+}$. Thus, for Fe^{2+} , k_2/k_{-1} is very high and becomes important only at high concentrations of Fe^{3+} . For Ce^{3+} , k_2/k_{-1} is approximately 10 and for Co^{3+} , the reverse step is predominant except at high concentrations of Co(II).

In view of the similarities of the bimolecular oxidations with $\text{S}_2\text{O}_8^{2-}$ ions and H_2O_2 , it may be appropriate to suggest a similar reverse step, viz.



The formation of the Fe(III) - sulfate ion pair eliminates the highly improbable termolecular step. The main point of interest here would be the comparison of k_{-1}/k_2 . From Uri's arguments, it seems that this ratio would probably be greater than that for Fe^{2+} and less than that for Ce^{3+} , taking

into account only the oxidation potentials of the systems. The nature of the radicals and factors such as the activation energies and entropies would affect profoundly the ratio of k_{-1}/k_2 in peroxydisulfate system. Nothing is known about these factors in these systems and so it is hard to speculate.

There is no a priori evidence for the reverse step but the observation that the deviation from the second order becomes more significant as the oxidation potential of the system decreases seems to encourage this suggestion. Further in the case of iron(II) complexes with bases such as phenanthroline, which are highly stable, Amphlett⁵ has shown that under suitable conditions Fe(III) is quantitatively reduced as a result of the γ radiolysis of water, whereas with simple Fe^{3+} , no reduction occurs. In the present investigation, the relative stabilities of the Fe(II) and Fe(III) complexes may also be a factor in determining the relative magnitudes of k_{-1} , and k_2 .

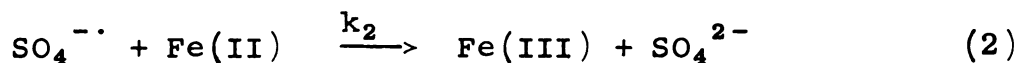
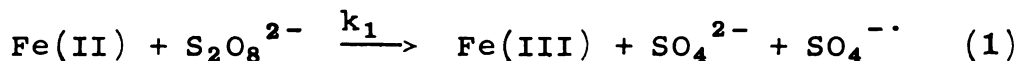
Although the deviation from the pseudo first order rate law suggests a probable reverse step, equilibrium was not observed due to the following difficulties; the reactions were carried out under conditions of large excesses of peroxydisulfate and on long term storage, the solutions became colorless due to hydrolysis or oxidation of the ligand by excess peroxydisulfate. However, when excess of Fe(II) complex was reacted with peroxydisulfate, the apparent stoichiometry measured from the decrease in absorptivity of

the Fe(II) complex solutions, showed that less than two equivalents of iron were being oxidized for each $S_2O_8^{2-}$ present. But in many cases, the iodometric titrations did not indicate any appreciable loss of peroxydisulfate to other reactions. It is tempting to infer the establishment of an equilibrium. However, the mixture could not be kept too long due to deterioration from other complications.

B. Role of Alcohol

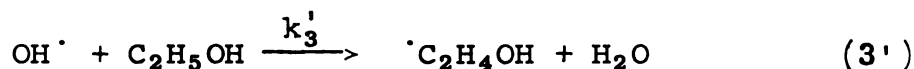
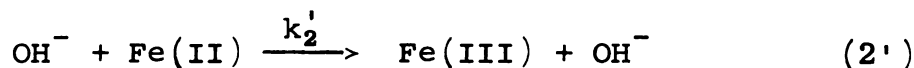
The results of the effect alcohol on the rate of oxidation of tris(bipyridine)-iron(II) indicated that the second step of oxidation is indeed due to the $SO_4^{\cdot -}$ radicals formed in the rate determining step and eliminated the possibility that $OH^{\cdot}$ radicals formed by the rapid equilibration $SO_4^{\cdot -} + H_2O \rightleftharpoons HSO_4^- + OH^{\cdot}$ may be the second stage oxidant. All these conclusions were reached from a direct comparison with a study of Kolthoff, Medalia and Raaen⁶⁸ on the peroxydisulfate - Fe^{2+} systems and the work of Merz and Waters⁸¹ as revised by Kolthoff, Medalia and Raaen,⁶⁸ on the relative rates of reaction of sulfate and hydroxyl radicals with Fe^{2+} and ethyl alcohol.

The role of alcohol in the tris(bipyridine)-iron(II)-sulfate-alcohol system has been explained on the basis of the following scheme of reactions:





Reactions (2), (3) and (4) are fast. The extent to which (2) and (3) occur depends upon the concentration of alcohol and Fe(II) and on the rate constants. k_3/k_2 , according to the calculations of Merz and Waters^{8,1} is equal to 0.0062 for the peroxydisulfate- Fe^{2+} system. This value was later revised by Kolthoff, et. al.⁶⁸ to 0.015. This ratio for the corresponding steps of the hydrogen peroxide- Fe^{2+} system namely



is 2.05. Assuming similar magnitudes for the tris(bi-pyridine)-iron(II)-peroxydisulfate system, there should be practically no reaction if the alcohol concentration is very much greater than Fe(II) concentration, on account of steps (3) and (4). Table IV gives the values for the rate constants at different concentrations of alcohol. It is evident from the data that at $[\text{alcohol}]/[\text{Fe(II)}]$ ratio greater than 2.4×10^3 (up to 1.9×10^5) there is very little overall oxidation of the Fe(II) complex, indicating that steps (3) and (4) predominate. At $[\text{alcohol}]/[\text{Fe}]$ ratios less than 2.0×10^2 the rate constant gradually increases to reach almost the value at zero alcohol concentration

when this ratio is about 21, indicating that step (2) dominates. If the $\text{OH}^\bullet$ radical is the second stage oxidant, then at this ratio for $[\text{alcohol}]/[\text{Fe(II) complex}]$, the corresponding step (3') should have been predominant by virtue of the much higher value for k_3'/k_2' . These results are very much in parallel to the work of Kolthoff, Medalia and Raaen⁶⁸ on the Fe(II) -peroxydisulfate system, and suggest that the sulfate radical is the reactive intermediate in these oxidations.

C. Mode of Electron Transfer

For a complicated system such as the one in the present investigation involving breaking of bonds in $\text{S}_2\text{O}_8^{2-}$ and where orbital overlaps may be important, it is hard to speculate whether an outer sphere or an inner sphere electron transfer occurs. It seems reasonable that a close contact between the Fe(II) complex and the peroxydisulfate ion may not be easy although it is sterically possible to accommodate the peroxydisulfate anion between the ligand molecules.²⁵ At the same time, the extensive delocalization of electrons in the π system of the ligands does not seem to play a very favorable role, if one compares the rates of oxidation of Fe^{2+} and the Fe(II) complexes with peroxydisulfate.⁴⁰ According to Marcus theory⁷⁴ for a series of reactions in which the enthalpy of activation is effectively constant and the coulombic interaction of the charges of the reactants are constant there should be a linear

relationship between the free energy of activation and the standard free energy of the oxidation-reduction step, with a slope of 0.5. The values of entropy in the present investigation differ quite a bit and hence no quantitative relationship could be expected. The linearity of the plot of ΔG^* versus ΔG^0 does, however, indicate that the free energy change of the oxidation-reduction step plays an important role in the rate of the reaction. In view of the complexities involved in the present investigation and also due to the standard deviation of about 2 kcal in the activation energies, much importance cannot be attached to the slope of this line. The value of the slope is, however, in agreement with Irvine's plot of $\log k$ versus the total change in the standard oxidation-reduction potential.

D. Activation Parameters

The reactions are all accompanied by extremely large negative values of entropies of activation, which is contrary to the value expected for reactions between positively and negatively charged species. These are much smaller than the $-8 \text{ cal}^0 \text{ K}^{-1} \text{ mol}^{-1}$ for the corresponding oxidation of Fe^{2+} by peroxydisulfate ion, and was not explained in the earlier work. Wilmarth and Haim¹⁰² have suggested that the small value of entropy of activation may be attributed to the long separation between the two species in the activated complex and thus making transfer of electrons by tunnelling over a considerable distance, a relatively

inefficient process. By contrast, the ferrous ion may come in closer contact with the peroxydisulfate ion in the activated complex which would contribute favorably to the entropy of activation in two ways, by reducing the electron transfer distance and by the loss of water from the solvation sphere of the Fe(II) ion.

The activation energies for these reactions is considerably lower than the value of 33.5 kcal required for the symmetrical fission of the peroxydisulfate ion.⁶⁹ Qualitatively, the lowering of the activation energy below the value of 33.5 kcal may be viewed as stabilization of the activated complexes caused by the partial transfer of electrons to the nascent sulfate radical ion.¹⁰² The increase in the free energy of activation with a decrease in the oxidation potential of the complex is compatible with this. The formation of a stable $\text{Fe(II)}-\text{S}_2\text{O}_8$ intermediate proposed in this investigation amounts to a delocalization of the electrons. The formation of this entity also qualitatively explains the low values of the entropy of activation. Separating these two steps, the calculated value for the ion pair formation step is obtained as about $+15 \text{ cal}^\circ \text{ K}^{-1} \text{ mol}^{-1}$ which is reasonable for such a process.

E. Effect of Substituents

The slope of the Hammett plot and the plot of $\log k$ versus pK_a indicates that the overall rate of the reaction is enhanced by withdrawal of electrons from the iron atom,

and is unexpected. However, a similar effect has been reported recently by Rund and Claus⁸⁸ for the catalytic decarboxylation of β -keto acids by the Mn(II) complexes of substituted phenanthrolines. The mechanism suggested is a similar one involving an equilibration and a breaking up of the intermediate complex.

LITERATURE CITED

1. Adam, F. C., and S. I. Weissman, J. Am. Chem. Soc. 80, 1518 (1958).
2. Afanasev, P. V., J. Phys. Chem. U.S.S.R. 9, 568 (1937).
3. Albery, W. J., Ann. Rep. Prog. Chem. (Chem. Soc.) 60, 40 (1963).
4. Amdur, I., and G. G. Hammes, "Chemical Kinetics", McGraw-Hill Book Company, New York. 1966.
5. Amphlett, C. B., Nature 165, 977 (1950).
6. Anderson, S., Acta Chem. Scand. 2, 1 (1948).
7. Ashurst, K. G., and W. C. E. Higginson, J. Chem. Soc. 3044 (1953).
8. Barb, W. G., J. H. Baxendale, P. George and K. R. Hargrave, Trans. Faraday Soc. 47, 462 (1951).
9. Barb, W. G., J. H. Baxendale, P. George, and K. R. Hargrave, Trans. Faraday Soc. 47, 591 (1951).
10. Barb, W. G., J. H. Baxendale, P. George, and K. R. Hargrave, Trans. Faraday Soc. 47, 935 (1955).
11. Basolo, F., J. C. Hayes, and H. M. Newmann, J. Am. Chem. Soc. 76, 3807 (1954).
12. Basolo, F. and R. G. Pearson, "Mechanisms of Inorganic Reactions", Second Edition. John Wiley and Sons Inc., 1967.
13. Bawn, C. E. H. and A. G. White, J. Chem. Soc. 331 (1951).
14. Bawn, C. E. H. and A. G. White, J. Chem. Soc. 339 (1951).
15. Bawn, C. E. H. and A. G. White, J. Chem. Soc. 343 (1951).
16. Bawn, C. E. H. and D. Margerison, Trans. Faraday Soc. 51, 925 (1955).
17. Baxendale, J. H. and P. George, Trans. Faraday Soc. 46, 736 (1950).

18. Bekier, E. and S. W. Kijowski, *Roczniki Chem.* 15,
136 (1935). *Chem. Abstracts* 30, 3306 (1936).
19. Benson, S. W., "The Foundations of Chemical Kinetics"
McGraw-Hill Book Co., New York. 1960.
20. Bhatnagar, S. S., B. Prakash, and J. Singh, *J. Indian
Chem. Soc.* 17, 133 (1940).
21. Brandt, W. W. and D. K. Gullstrom, *J. Am. Chem. Soc.*
74, 3532 (1952).
22. Brubaker, C. H. (Jr.), *Record of Chemical Progress*
24, 181 (1963).
23. Burgess, J. and R. H. Prince, *J. Chem. Soc.* 5752 (1963).
24. Burgess, J. and R. H. Prince, *J. Chem. Soc.* 4697 (1965).
25. Burgess, J. and R. H. Prince, *J. Chem. Soc.* 1772 (1966).
26. Campion, R. J., N. Purdie, and N. Sutin, *Inorg. Chem.*
3, 1091 (1964).
27. Chaltykyan, O. A. and N. M. Beilerian, *Izvest. Akad.
Nauk Armian S.S.R., Khim. Nauki.* 11, 13 (1958).
Chem. Abstracts 53, 1902 (1959).
28. Chlebek, R. W. and M. W. Lister, *Can. J. Chem.* 45,
2411 (1967).
29. Cone, W. H., *J. Am. Chem. Soc.* 67, 78 (1945).
30. Csayni, L. J. and F. Solymosi, *Acta Univ. Szegediensis,
Acta Phys. et Chem.* 5, 34 (1959). *Chem. Abstracts*
54, 13924 (1960).
31. Deck, C. F., and A. C. Wahl, *J. Am. Chem. Soc.* 76,
4054 (1954).
32. Dekker, A. O., H. A. Levy, and D. M. Yost, *J. Am. Chem.
Soc.* 59, 2129 (1937).
33. Dickens, J. E., F. Basolo, H. M. Neumann, *J. Am. Chem.
Soc.* 79, 1286 (1957).
34. Diebler, H. and N. Sutin, *J. Phys. Chem.* 68, 174 (1964).
35. Downs, J. and R. E. Johnson, *J. Chem. Phys.* 22, 143
(1954).
36. Dulz, G. and N. Sutin, *Inorg. Chem.* 2, 917 (1963).

37. Eichler, E. and A. C. Wahl, J. Am. Chem. Soc. 80, 4145 (1958).
38. Evans, M. G. and N. Uri, Nature 166, 602 (1950).
39. Evans, M. G. and N. Uri, "Symposium No. 5, Carbon dioxide Fixation and Photo-synthesis, Society of Experimental Biology, Sheffield", 1950, p. 130, Cambridge.
40. Fordham, J. W. L. and H. L. Williams, J. Am. Chem. Soc. 73, 1634, 4855 (1951).
41. Ford-Smith, M. H. and N. Sutin, J. Am. Chem. Soc. 83, 1830 (1961).
42. Frazer, R. T. M., Rev. Pure Appl. Chem. (Australia) 11, 64 (1961).
43. French, T. C. and T. C. Bruice, Biochemistry 3, 1589 (1964).
44. Fronaeus, S. and C. O. Ostman, Acta Chem. Scand. 10, 320 (1956).
45. Frost, A. A. and R. G. Pearson, "Kinetics and Mechanisms" Second Edition, John Wiley and Sons, New York. 1961.
46. Galiba, H., L. J. Csanyi, and Z. G. Szalo, Z. Anorg. Allgem. Chem., 287, 169 (1956).
47. Garrick, F. J., Trans. Faraday Soc. 33, 486 (1937).
48. George, P. and D. H. Irvine, J. Chem. Soc. 587 (1954).
49. Gupta, Y. K. and S. Ghosh, J. Inorg. Nuclear Chem. 9, 178 (1959).
50. Haim, A. and H. Taube, J. Am. Chem. Soc. 85, 3108 (1963).
51. Haim, A. and W. K. Wilmarth, J. Am. Chem. Soc. 83, 509 (1961).
52. Halpern, J., Quart. Rev. 15, 207 (1961).
53. Halpern, J. and L. Orgel, Discussions Faraday Soc. 29, 32 (1960).
54. Harkness, A. C. and J. Halpern, J. Am. Chem. Soc. 81, 3526 (1959).

55. Holluta, J. and W. Hermann, Z. Physik. Chem. 166A, 453 (1933).
56. House, D. A., Chem. Rev. 62, 185 (1962).
57. Hudis, J. and R. W. Dodson, J. Am. Chem. Soc. 78, 911 (1956).
58. Hush, N. S., Trans. Faraday Soc. 57, 557 (1961).
59. Irvine, D. H., J. Chem. Soc. 1841 (1957).
60. Irvine, D. H., J. Chem. Soc. 2166 (1958).
61. Irvien, D. H., J. Chem. Soc. 2977 (1959).
62. Jaffè, H. H., Chem. Rev. 53, 191 (1953).
63. Jirsa, F., Z. Anorg. Allgem. Chem. 148, 130 (1925). and 158, 33 61 (1926).
64. King, C. V., J. Am. Chem. Soc. 49, 2689 (1927).
65. King, C. V., J. Am. Chem. Soc. 50, 2080, 2089 (1928).
66. King, C. V., and F. L. Griswold, J. Am. Chem. Soc. 52, 1493 (1930).
67. Kolthoff, I. M. and R. Belcher, "Volumetric Analysis (III)", Interscience Publishers, New York, 1957, p. 288.
68. Kolthoff, I. M., A. I. Medalia and H. P. Raaen, J. Am. Chem. Soc. 73, 1733 (1951).
69. Kolthoff, I. M. and I. K. Miller, J. Am. Chem. Soc. 73, 3055 (1951).
70. Kolthoff, I. M., P. R. O'Connor, J. L. Hanson, J. Polymer Sci. 15, 459 (1955).
71. Latimer, W. M., "The Oxidation States of the Elements, and their Potentials in Aqueous Solution", Prentice Hall, New York, N.Y., 1952, p. 78.
72. Libby, W. F., J. Chem. Phys. 38, 420 (1963).
73. Marcus, R. A., J. Chem. Phys. 24, 966 (1956); 26, 867 (1957); 26, 872 (1957).
74. Marcus, R. A., J. Phys. Chem. 67, 853 (1963).
75. Marcus, R. A., Can. J. Chem. 37, 155 (1964).

76. Marcus, R. A., Ann. Rev. Phys. Chem. 15, 155 (1964).
77. Marcus, R. A., J. Chem. Phys. 43, 679 (1965).
78. Marcus, R. J., B. Zwolinski, and H. Eyring, J. Phys. Chem., 58, 432 (1954).
79. Marshall, H., Proc. Roy. Soc. (edinburgh) 23, 163 (1900).
80. McDaniel, D. H. and H. C. Brown, J. Org. Chem. 23, 42 (1958).
81. Merz, J. H. and W. A. Waters, Discussions Faraday Soc. 2, 179 (1947).
82. Nordmeyer, F. and H. Taube, J. Am. Chem. Soc. 90, 1162 (1968).
83. Noyes, A. A., J. L. Hoard and K. S. Pitzer, J. Am. Chem. Soc. 57, 1221 (1935).
84. Noyes, A. A. and A. Kossiakoff, J. Am. Chem. Soc. 57, 1238 (1935).
85. Noyes, A. A., D. De Vault, C. D. Coryell, and T. J. Deahl, J. Am. Chem. Soc. 59, 1326 (1937).
86. Perlmutter-Hayman, B., and G. Stein, J. Chem. Phys. 40, 848 (1964).
87. Raman, S. (Unpublished results)
88. Rund, J. V., and K. G. Claus, Inorg. Chem. 7, 860 (1968).
89. Simon, A., W. Haufe, Th. Reetz, and R. Preisler, Z. Anorg. Chem. 230, 129 (1936).
90. Sloth, E. N. and C. S. Garner, J. Am. Chem. Soc. 77, 1440 (1955).
91. Smith, W. V., J. Am. Chem. Soc. 71, 4077 (1949).
92. Stoner, P., M.S. Thesis, Michigan State University, 1966.
93. Stranks, D. R., Discussions Faraday Soc. 29, 73 (1960).
94. Sutin, N., Ann. Rev. Nucl. Sci. 13, 285 (1962).
95. Taube, H., Progress in Inorg. and Nuclear Chem. 1, 1(1959).
96. Uri, N., Chem. Rev. 50, 375 (1951).

97. Wang, J. H., and W. S. Brinigar, Proc. Natl. Acad. Sci., 46, 958 (1960).
98. Weiss, J., Experientia 7, 135 (1951).
99. Wells, C. F. and M. A. Salam, Nature 203, 751 (1964).
100. Wells, C. F. and M. A. Salam, Trans. Faraday Soc. 63, 620 (1967).
101. Wells, C. F. and M. A. Salam, J. Chem. Soc. (A), 308 (1968).
102. Wilmarth, W. K. and A. Haim, "Peroxide Reaction Mechanisms", Interscience Publishers, London (1961) p. 175.
103. Yost, D. M., J. Am. Chem. Soc. 48, 152 (1926).
104. Yost, D. M., J. Am. Chem. Soc. 48, 374 (1926).
105. Yost, D. M., and W. H. Claussen, J. Am. Chem. Soc. 53, 3349 (1931).
106. Zwickel, A. M. and H. Taube, Discussions Faraday Soc. 29, 42 (1960).

APPENDIX

The rate constants calculated from the different experiments are summarized in the following tables. The averages of these rate constants were used for further calculations of the forward rate constants, graphically. In some cases, the readings, which appeared obviously out of line with the others, were not considered in computing the average. Most of these were in the case of 5-nitro- and 5-chloro-phenanthroline complexes, where a small delay in starting the runs, caused a serious difference and a few were traced back to faulty temperature control.

Temp. °C	$[S_2O_8^{2-}] \times 10^3 (M)$	Second Order Rate Constants ($M^{-1}sec^{-1}$) $\times 10^1$
<u>Tris</u> -(2,2'-Bipyridine)-iron(II) sulfate		
25	1.0	3.34, 3.47, 3.37, 3.22
	1.5	2.88, 2.93
	2.0	2.69, 2.69, 2.72
	2.5	2.48, 2.50, 2.46
	3.0	2.33, 2.35, 2.34, 2.29
	4.0	2.14, 2.13, 2.14, 2.15
	5.0	1.85, 1.92
30	1.0	4.54, 4.69, 4.32
	2.0	3.46, 3.46, 3.48, 3.48
	2.5	3.34, 3.34
	3.0	3.12, 3.12, 3.08, 2.98, 2.98
	3.5	3.06, 3.06
	4.0	2.71, 2.80, 2.43, 2.96, 2.96
	5.0	2.6
35	1.0	5.48, 5.45, 5.53, 5.54
	1.5	4.78
	2.0	4.50, 4.43, 4.31, 4.51
	2.5	4.18, 4.12
	3.0	3.83, 3.75, 3.63
	4.0	3.53, 3.53, 3.41
40	1.0	7.11, 7.15, 7.06, 7.2, 7.1
	1.5	6.34, 6.41
	2.0	5.6, 5.4, 5.25, 5.49, 5.65, 5.75
	2.5	5.17, 5.40, 5.01
	3.0	4.62, 4.62, 4.71, 5.1, 4.31
	4.0	4.08, 4.03, 4.06

Temp. °C	[S ₂ O ₈ ²⁻] x 10 ³ (M)	Second Order Rate Constants (M ⁻¹ sec ⁻¹) x 10 ¹
<u>Tris-(1,10-Phenanthroline)-iron(II) sulfate</u>		
25	1.0	1.69, 1.70, 1.81, 1.80, 1.81, 1.62
	2.0	1.31, 1.29, 1.39, 1.21, 1.30
	3.0	1.23, 1.26, 1.31, 1.41
	4.0	1.01, 1.01, 1.02, .98, 1.13
30	1.0	2.33, 2.27, 2.3, 2.76
	2.0	1.98, 1.92, 1.92, 1.88
	3.0	1.73, 1.71, 1.73, 1.81
	3.5	1.60, 1.71, 1.60
	4.0	1.54, 1.54, 1.56, 1.51, 1.66
	4.5	1.44, 1.43
	5.0	1.17, 1.18
35	1.0	3.47, 3.41, 3.29, 3.49, 3.38, 3.22
	1.5	3.1, 2.98
	2.0	2.63, 2.57, 2.63, 2.73, 2.93, 2.32
	2.5	2.33, 2.28
	3.0	2.25, 2.19, 2.27, 2.35, 2.14, 2.34
	4.0	1.97, 1.97, 2.01, 1.81
	4.5	1.91
40	1.0	4.16, 4.21, 4.54, 3.95, 4.28
	1.5	3.34, 3.36
	2.0	3.05, 3.03, 3.17, 3.11, 3.21
	3.0	2.61, 2.61, 2.63, 2.91, 2.31
	4.0	2.26, 2.30, 2.31, 2.16

Temp. °C	$[S_2O_8^{2-}] \times 10^3 (M)$	Second Order Rate Constants $(M^{-1}sec^{-1}) \times 10^0$
<u>Tris-(4,4'-Dimethyl-2,2'-bipyridine)-iron(II) sulfate</u>		
25	0.5	4.59, 4.75, 4.76, 4.58
	1.0	3.55, 3.56, 3.54
	1.5	3.07, 3.10, 3.06
	2.0	2.67, 2.81
30	0.5	6.02, 6.26, 5.82
	1.0	5.24, 5.07
	1.5	3.84, 3.84
	2.0	3.09, 3.36
	2.5	3.22, 2.97
35	0.5	6.96, 6.91
	1.0	5.43, 5.49, 5.81
	1.5	4.74, 4.62, 4.21
	2.0	4.32, 3.76
40	0.5	8.15, 8.05
	1.0	6.40, 6.62, 5.86, 7.12
	1.5	4.84, 5.05
		$(M^{-1}sec^{-1}) \times 10^2$
<u>Tris-(5-Methyl-1,10-phenanthroline)-iron(II) sulfate</u>		
25	1.0	6.97, 6.72, 7.51, 6.12
	2.0	6.25, 5.83, 5.62, 5.08, 5.92, 6.31
	3.0	5.41, 5.50, 5.52, 5.4, 4.65, 4.26, 4.51
	4.0	4.3, 4.26, 4.35, 4.61, 4.12

Temp. °C	[S ₂ O ₈ ²⁻] x 10 ³ (M)	Second Order Rate Constants (M ⁻¹ sec ⁻¹) x 10 ²
30	1.0	11.8, 10.5, 12.4, 10.1, 12.1
	1.5	9.4, 9.4
	2.0	8.5, 8.3, 7.95, 8.82, 7.62, 9.31
	2.5	7.11, 7.32, 7.60
	3.0	6.67, 6.91, 6.83
	4.0	6.01, 6.01, 5.97
35	1.0	13.6, 12.4, 12.5, 13.0, 13.4
	1.5	11.4, 12.1
	2.0	11.1, 10.8, 10.1, 12.5
	2.5	10.0
	3.0	9.46, 9.48, 10.3, 10.4, 8.64, 8.95
	4.0	8.53, 8.29, 8.36, 8.86, 8.11
40	1.0	$\frac{(M^{-1}sec^{-1}) \times 10^1}{1.95, 2.00, 2.08, 2.22, 1.75}$
	1.5	1.7, 1.77, 1.84
	2.0	1.34, 1.26, 1.41, 1.50, 1.3
	2.5	1.21
	3.0	1.11, 1.05, 1.09, 1.11, 1.08, 1.21
	4.0	1.02, 1.06, 1.12, .993
		$\frac{(M^{-1}sec^{-1}) \times 10^2}{}$
<u>Tris</u> -(5-Chloro-1,10-phenanthroline)-iron(II) sulfate		
25	1.0	9.45, 9.33, 9.69
	2.0	4.78, 4.94, 5.54, 5.02, 4.51, 4.5, 5.35
	3.0	3.29, 3.62, 3.76, 3.69, 3.71, 3.82, 3.39, 3.29
	4.0	2.79, 2.78, 2.95, 2.86, 2.91, 2.72

Temp. °C	$[S_2O_8^{2-}] \times 10^3 (M)$	Second Order Rate Constants $(M^{-1}sec^{-1}) \times 10^2$
30	1.0	22.4, 23.4, 20.7, 22.2
	2.0	9.15, 9.10, 9.0, 10.1, 8.2, 10.1, 8.3
	3.0	6.77, 6.97, 6.90, 6.71
	4.0	4.21, 5.03, 4.32, 6.51, 4.93, 5.83
		$(M^{-1}sec^{-1}) \times 10^1$
35	1.0	3.45, 2.3, 3.99, 2.7, 4.1, 2.21
	2.0	1.91, 2.0, 1.81, 2.21, 1.72, 2.31
	3.0	1.23, 1.34, 1.17, 1.02, 1.38, 1.21
	4.0	.96, .95, .98, .92, .91, 1.06
40	1.0	5.21, 5.13, 5.26, 5.17
	2.0	3.43, 3.31, 2.62, 2.91, 2.61
	3.0	1.81, 2.20, 2.39, 2.06, 1.92, 1.90, 2.21
	4.0	1.75, 1.83, 1.93, 1.72
<u>Tris</u> -(5-Nitro-1,10-phenanthroline)-iron(II) sulfate		
25	1.0	1.55, 1.78, 1.62, 1.72, 1.85, 1.79
	1.5	1.13, 1.31
	2.0	.82, .88, .92, .85, .78, .73, .91
	2.5	.69, .71, .71
	3.0	.61, .55, .65, .62, .64, .54
	4.0	.45, .46, .43, .49, .42, .48
30	1.0	3.97, 3.5, 3.61, 4.01, 4.71
	2.0	2.06, 2.06, 1.97, 1.72, 2.31
	3.0	1.59, 1.47, 1.21, 1.84
	4.0	1.04, 1.1, .96, .92, 1.2, 1.01

Temp. °C	$[\text{S}_2\text{O}_8^{2-}] \times 10^3 (\underline{\text{M}})$	Second Order Rate Constants $(\text{M}^{-1}\text{sec}^{-1}) \times 10^1$
35	1.0	5.41, 5.43, 5.52, 5.34
	2.0	3.15, 3.09, 3.21, 3.05
	3.0	2.49, 2.17, 2.34, 2.71, 2.61
	4.0	1.51, 1.62, 1.74, 1.74
40	1.0	7.81, 9.5, 8.1, 8.0, 7.5, 10.8
	2.0	5.55, 5.53, 5.13, 5.25, 5.91
	3.0	3.83, 3.75, 3.74, 3.52, 3.96
	4.0	3.01, 3.04, 3.03, 3.12, 2.98

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03175 7598