12-1975

Anion Assisted Redox Rates Between Cobalt (II) - Cobalt (III) Polypyridyl Complexes in Acetophenone

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Recommended Citation

Garmestani, Seyed, "Anion Assisted Redox Rates Between Cobalt (II) - Cobalt (III) Polypyridyl Complexes in Acetophenone" (1975). *Masters Theses & Specialist Projects.* Paper 2394.
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ANION ASSISTED REDOX RATES BETWEEN COBALT(II)-COBALT(III) POLYPYRIDYL COMPLEXES IN ACETOPHENONE

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Seyed K. Garmestani
December 1975

ANION ASSISTED REDOX RATES BETWEEN COBALT(II)-COBALT(III) POLYPYRIDYL COMPLEXES IN ACETOPHENONE

APPROVED December 10, 1975 :
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ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. Robert D. Farina for his guidance in this research project, and for his valuable assistance during the writing of this thesis. I am also indebted to Dr. Norman L. Holy for the use of his equipment and research facilities during my research period. Finally, I would like to thank the members of the chemistry department for the fine instruction I received during my graduate studies here.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ANION ASSISTED REDOX RATES BETWEEN COBALT(II)-COBALT(III) POLYPYRIDYL COMPLEXES IN ACETOPHENONE

Seyed K. Garmestani December 1975 40 pages

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The effects of ionic strength and various anions on the rate of electron transfer between tris(2,2'-dipyridine) cobalt(III) and bis(2,2',2"-tripyridine) cobalt(II) complexes have been examined in acetophenone. The redox rate was found to increase with increasing ionic strength in both the presence and absence of added salts. The reaction was first order with respect to each reactant and second order overall in all cases. The influence of the ClO_4^-, BF_4^-, and $B(C_6H_5)_4^-$ anions on the reaction rate was studied with their order of effectiveness being: $ClO_4^- > BF_4^- >> B(C_6H_5)_4^-$.

The reverse trend occurs in their ion pairing properties where the large size of the $B(C_6H_5)_4^-$ anion exerts a much stronger tendency to form ion pairs with the large reactant cations than either of the ClO_4^- and BF_4^- species. The proposed rate law in the presence of the ClO_4^- and BF_4^- anions was as follows:

$$\text{Rate} = k_x[Co(dipy)_3^{3+}][Co(tripy)_2X^+]$$

where the rate is independent of the anion concentration. An alternate rate law was proposed for the $B(C_6H_5)_4^-$ anion where a greater degree of ion pairing was obtained. In the absence of added salts, the redox rate is believed to occur by two different reaction pathways.

Activation parameters were determined for each salt system as well as in the absence of added salts at $\mu = 0.0027$ M and over a temperature range of 25-41°C. Factors affecting the activation parameters are discussed.

STATEMENT OF THE PROBLEM

Previous studies of the redox rates between cobalt(II)-cobalt(III) polypyridyl complexes in a number of nonaqueous solvents have shown that the fastest rate occurs in acetophenone. Therefore, this study was undertaken to examine some of those factors which influence the redox rate between transition metal complexes in the nonaqueous solvent, acetophenone. The system selected for study involved the reduction of tris(2,2'-dipyridine)cobalt(III) by the bis(2,2',2"-tripyridine)cobalt(II) complex which has been previously examined in aqueous solution at relatively high ionic strength. This study was made at relatively low ionic strength conditions in the presence of perchlorate, tetrafluoroborate, and tetraphenylborate anions. The results of these studies were used to determine the rate law, reaction mechanism, reactant species and the degree of ion pairing in the different anion solutions. The redox rate constants were obtained by spectrophotometric techniques under pseudo-first order conditions. The overall reaction order was determined as well as the order with respect to each reactant. Rate constants and activation parameters were determined for all salt solutions over a temperature range of 25-41°C. Visible spectra of each reaction component and the equilibrium constant for this system were determined in acetophenone.

INTRODUCTION

Numerous studies have been made on the electron transfer reactions of transition metal complexes in aqueous solution. However, there have been substantially fewer studies made of these reactions in nonaqueous solvents. The elucidation of the mechanisms of redox reactions between metal complex ions and the factors which influence their rate are much more complex than is suggested by the simple equations which represent their reactions. After an extensive study of this class of reactions, two principal mechanisms evolve termed inner-[1-3] and outer-sphere.[4, 5] Both are discussed thoroughly in the literature. A brief description of each reaction mechanism with pertinent examples follows.

A. Inner-Sphere Redox Reactions

Redox reactions which proceed by an inner-sphere mechanism have the central metal ion of both oxidant and reductant sharing a common ligand in the activated complex during the electron transfer. Support for this mechanism has been obtained through analysis of the reaction products since the electron transfer is usually accompanied by the transfer of the bridging ligand from oxidant to reductant. The first such example was reported by Taube and Myers[6] who examined the redox reaction between $Co(NH_3)_5Cl^{2+}$ and $Cr(OH_2)_6^{2+}$ where the analysis of the reaction products yielded $Cr(OH_2)_5Cl^{2+}$ instead of $Cr(OH_2)_6^{3+}$. From this analysis and the knowledge of the substitution lability of the $Cr(OH_2)_6^{2+}$ species, they proposed that the chloride group is coordinated to both the cobalt and chromium complexes in the activated complex. After the electron transfer is complete and the activated complex dissociates, the chloride ion remains attached to Cr(III).

The effects of anions (primarily halide ions) have been examined on a number of inner-sphere redox reactions in water but there have been no cation effects reported to date. An example of the former involves the redox reaction between $Co(NH_3)_5FuH^+$ and $Cr(OH_2)_6^{2+}$ where FuH^- is defined as the fumarate anion ligand. In the absence of halides, the reaction product is $Cr(OH_2)_5FuH^{2+}$ whereas at high concentrations of halide, the $XCr(OH_2)_4FuH^+$ species forms.[7] The rate constant expression associated with this reaction is:

$$k_{obs} = k_o + k_x[X^-] \qquad (1)$$

where k_o is the rate constant in the absence of halide ions, k_x is the rate constant in the presence of halide ions and $[X^-]$ is the halide ion concentration. The identical equation for the rate constant was obtained in both the $Co(NH_3)_5OH_2^{3+}$ - $V(OH_2)_6^{2+}$ and $Cr(OH_2)_5Cl^{2+}$ - $Cr(OH_2)_6^{2+}$ systems.[8, 9] King et al[10] have examined the influence of the perchlorate ion on the latter system and found that the rate law was as follows:

$$\text{Rate} = k\,[CrCl^{2+}][Cr^{2+}][ClO_4^-]\,a_w^{-1} \qquad (2)$$

where a_w is the activity of water.

Anion effects on inner-sphere redox reactions have also been studied in nonaqueous solvents using the complexes of Fe(II) and Fe(III) as model systems. Menashi and coworkers[11] examined an Fe(II)/Fe(III) system in DMSO where the $Fe[OS(CH_3)_2]_6^{2+}$ and $Fe[OS(CH_3)_2]_6^{3+}$ complexes form. The mechanism proposed for the electron transfer involves the attachment of one iron ion to the oxygen end and the other iron ion to the sulfur end of an S-0 bond. Introduction of anions to the system enhanced the reaction rate due to the formation of $Fe(DMSO)_5X^{2+}$ and $Fe(DMSO)_4X_2^+$ species which reduce the coulombic repulsion upon formation of the activated complex.[12, 13] Moreover, it was proposed that the anions served as bridging groups which also would tend to enhance the rate of electron transfer. Similar results were obtained in N,N-dimethylformamide when chloride was added to the Fe(II)/Fe(III) system and $FeCl^{2+}$ as well as $FeCl_2^+$ species were formed.[14] The influence of perchloric acid on this system was also examined and found to decrease the redox rate.

B. Outer-Sphere Redox Reactions

In outer-sphere redox reactions, electron transfer occurs through the intact coordination shells of both metal complex ions and involves changes in both the inner- and outer-sphere environment of the complex. In this mechanism, bonds are neither formed nor cleaved. There are numerous instances in which it seems reasonably clear that an outer-sphere mechanism must be operating in the electron transfer reaction. The established crieteria for an outer-sphere mechanism are that the reactants are substitution inert complexes or that all coordination sites of the central metal ion are occupied by ligands with the electron transfer faster than the rate of ligand substitution e.g. the $Co(tripy)_3^{2+}$ - $Co(phen)_3^{3+}$ system.[15]

The electron exchange between Fe(II)/Fe(III) complexes with various ligands and its catalysis by various cations has been extensively studied in aqueous solution and even in some nonaqueous solvents. Sutin and Gordon[16] studied the effect of perchloric acid on the rate of reaction between tris(1,10-phenanthroline)-iron(II), $Fe(phen)_3^{2+}$ and tris(1,10-phenanthroline)-iron(III), $Fe(phen)_3^{3+}$. It was found that the rate of reaction increases with decreasing acid concentration. The formation of the $HFe(phen)_3^{4+}$ species at high concentrations of acid was proposed where this species reacts more slowly with $Fe(phen)_3^{2+}$ than $Fe(phen)_3^{3+}$ due to the increased coulombic repulsion. Another example of an outer-sphere redox reaction involves the electron exchange reaction between FeY^{-2} and FeY^{-1} where Y^{-4} is the ethylenediaminetetraacetic acid anion ligand. It was demonstrated[17] that the reaction occurs primarily between the deprotonated FeY^{2-} and FeY^{1-} complexes rather than between any protonated species even at a pH of 2.

The effect of cations on the redox rate between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ has been examined.[18] The order of effectiveness with various cations is found to be: $Cs^+ > Rb^+ > K^+$; $NH_4^+ > Na^+ > Li^+ > H^+$; and $Sr^{2+} > Ca^{2+} > Mg^{2+}$. These trends suggest that cationic size is an important factor influencing the rate of electron transfer. It has been proposed that the metals act as outer-sphere bridges and the activated complex has a configuration as follows:

$$[Fe(CN)_6 \cdot \cdot \cdot M \cdot \cdot \cdot Fe(CN)_6]^{-7+n}$$

where M = metal ion and n is its oxidation state. Wahl and coworkers[19] have investigated the effect of tetraalkylammonium cations on the rate of this reaction. The large and specific effects of cations on the rate of reaction strongly suggests that the cation participates in the reaction by reducing the repulsive forces through ion pair formation. Ion pair formation is also suggested by N.M.R. measurements.[20]

Anions can also affect redox reactions of the outer-sphere type. One such example involves the $Fe(C_2H_5)_2/Fe(C_2H_5)_2^+$ system which has been studied in aqueous[21, 22] and nonaqueous solvents.[23] In methanolic solutions, the rate constants are the same for ferricinium nitrate and perchlorate. However, with the chloride salt, the rate is immeasurably faster even at -75°C. Thus, certain "inert" electrolytes may or may not influence the rate similarly.

The effect of several anions on the rate of reduction of both $Fe(phen)_3^{3+}$ and $Fe(dipy)_3^{3+}$ by the ferrous ion has been examined by Sutin.[24] The added anions appeared to influence the reaction rate quite differently with the observed rate constant showing either a first or second order dependence on the anion concentration. The rate law for this reaction is as follows:

$$\text{Rate} = k_{obs}[Fe(phen)_3^{3+}][Fe^{2+}] \qquad (3)$$

Taube et al[8] have examined the effect of halides on the reaction rate between $Cr(OH_2)_6^{2+}$ and $Co(NH_3)_6^{3+}$. The expression for the observed rate constant is the same as equation (1) discussed earlier in this section. Identical expressions for the rate constant were also obtained in the reduction of $Co(NH_3)_6^{3+}$ and $(NH_3)_5CoNH_2Co(NH_3)_5^{6+}$ by $V(OH_2)_6^{2+}$.[7, 25] However, in the latter system, the equation for the rate constant when either sulfate or fluoride was present is of the form:

$$k_{obs} = k_o + k_1[X^-] + k_2[X^-]^2$$

Sutin[26] has examined the effect of different anions on the redox reaction between $Fe(OH_2)_6^{3+}$ and $Co(phen)_3^{2+}$ in water where the anions appear to enhance the reaction rate through ion pairing with $Fe(OH_2)_6^{3+}$. This behavior is analogous to the Fe(II)/Fe(III) system in N,N-dimethylformamide when chloride was added. Baker et al[27] have examined the effect of Cl^- and NO_3^- on the electron exchange between $Co(phen)_3^{3+}$ and $Co(phen)_3^{2+}$ in water and found that the reaction is first order with respect to each reactant in the presence of NO_3^- but in Cl^- solutions, the reaction is first order with respect to the oxidant and approximately 1/2 order with respect to the reductant. Ion pair formation between $Co(phen)_3^{3+}$ and Cl^- was postulated with the proposed reaction mechanism being:

$$Co(phen)_3^{3+} \cdot \cdot \cdot Cl^- \xrightarrow[slow]{k_1} Co(phen)_3^{3+} + Cl^- \qquad (5)$$

$$Co(phen)_3^{3+} + Co(phen)_3^{2+} \xrightarrow{k_2} \text{product} \qquad (6)$$

Assuming that the ion pair dissociation is slow compared to the redox reaction, this would account for the fractional dependence of the reductant on the reaction rate. The reasons cited for the slow dissociation were related to the structural characteristics of the phenanthroline complex.

In summary, the rate of electron exchange between transition metal complexes can be very sensitive to the presence of added counter ions in the solution. Frequently, added anions exert a great influence on the rate of reaction between two cation reactants while added cations have similar effects on the rate of reaction between two anion reactants. The catalytic effect of a counter ion can have at least two explanations:

a. The ion facilitates approach of similarly charged reactants through ion pairing which lowers their charge and hence reduces the repulsive forces between reactants prior to the electron transfer.

b. The counter ion can serve as a bridge between reactants in the activated complex.

In this study, the effects of ionic strength, temperature, and different anions on the redox reaction between tris(2,2'-dipyridine) cobalt(III) and bis(2,2',2"-tripyridine)cobalt(II) were examined in acetophenone. The results of this study have been used to determine the anion effect, rate law, reaction mechanism, reactant species, degree of ion pairing, and activation parameters on an outer-sphere redox reaction in a nonaqueous solvent.

EXPERIMENTAL

This section contains the following parts: materials, apparatus, kinetics, equilibrium study and preliminary experiments.

A. Materials

All materials were used without further purification unless otherwise noted.

1. Cobalt(II)-Cobalt(III) Polypyridyl Complexes

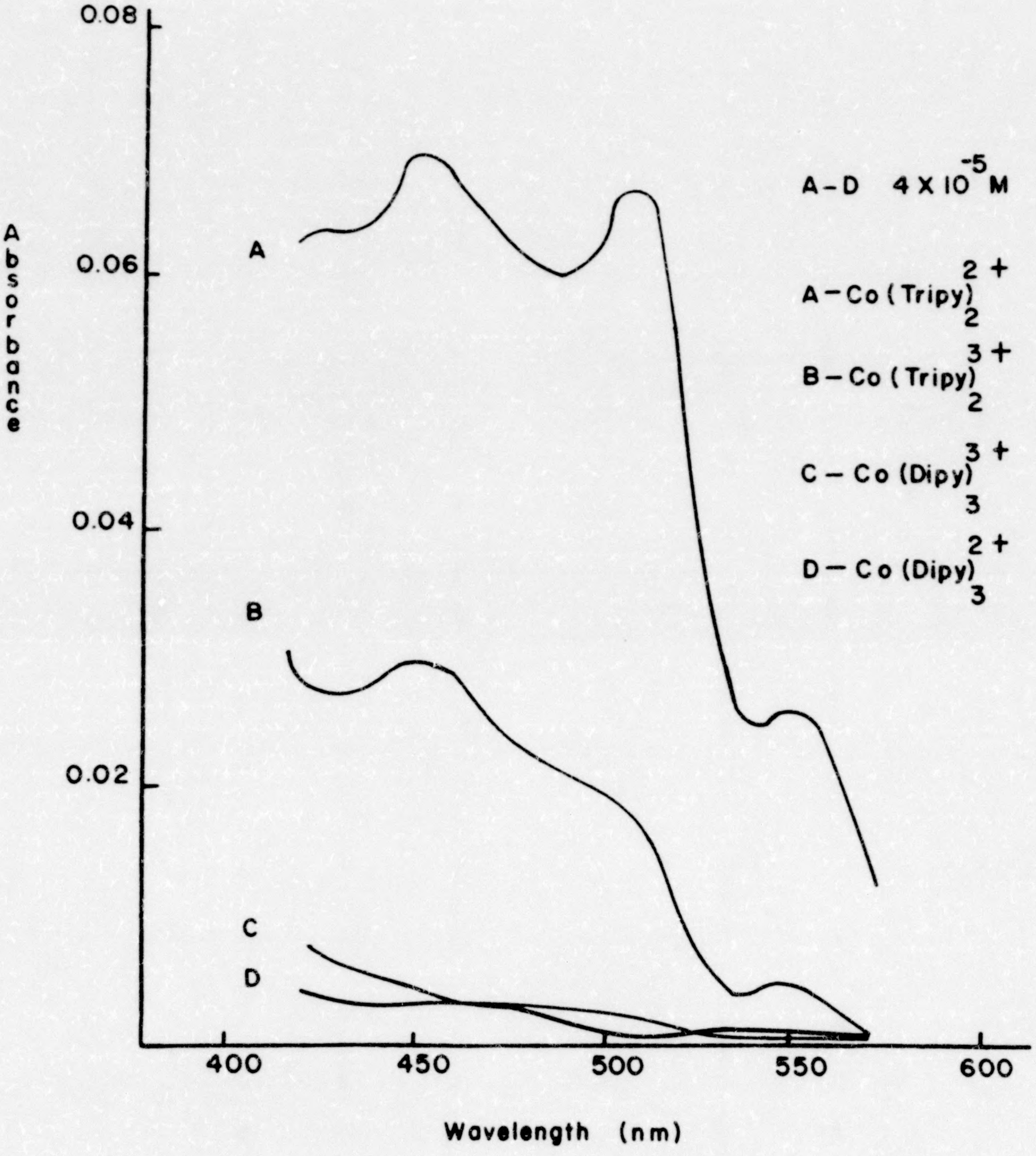
The ligands, dipyridine and tripyridine were purchased from Matheson, Coleman and Bell as well as the G. F. Smith chemical company. They were reagent grade and purified by vacuum sublimation as described in the literature.[15, 28] The $CoCl_2 \cdot 6H_2O$ which was the cobalt source for the preparation of the reaction components in this study was reagent grade and obtained from the Matheson, Coleman and Bell chemical company.

The visible spectra of the reaction components in acetophenone are presented in Figure 1. No ultraviolet spectra could be taken since the cutoff wavelength of acetophenone was found to be 380 nm.[29]

a. $Co(dipy)_3(ClO_4)_3 \cdot 3H_2O$

This compound was prepared by following the procedure of Burstall and Nyholm.[30] The ultraviolet spectrum of the complex in water was in agreement with that obtained by Waind and Martin.[31] Since this complex has no appreciable visible spectra and acetophenone is opaque in the ultraviolet region of the light spectrum, no spectral results could be obtained.

Figure 1. Visible Spectra of Reaction Components in Acetophenone


Absorbance
0.08
0.06
0.04
0.02
400
450
500
550
600
Wavelength (nm)
A
B
C
D
A-D 4×10^{-5} M
A – $Co(Tripy)_2^{2+}$
B – $Co(Tripy)_2^{3+}$
C – $Co(Dipy)_3^{3+}$
D – $Co(Dipy)_3^{2+}$

b. $Co(tripy)_2(ClO_4)_2 \cdot H_2O$

The complex was prepared by following the method used by Basolo et al.[27] The visible spectrum of the complex in water is consistent with the literature.[32] Absorption maxima with their corresponding wavelengths in acetophenone at 25°C are presented below:

Wavelength(Å)	Molar Absorptivity ($M^{-1}cm^{-1}$)
$\lambda_1 = 5500$	478
$\lambda_2 = 5090$	1261
$\lambda_3 = 4500$	1391

c. $Co(dipy)_3(ClO_4)_2$

This compound was prepared as described in reference 30. The ultraviolet spectrum of this compound in water is the same as that obtained by Schlafer.[33] No spectral data could be obtained in acetophenone for the same reasons given above in the discussion of the analogous $Co(dipy)_3(ClO_4)_3 \cdot 3H_2O$ complex.

d. $Co(tripy)_2(ClO_4)_3 \cdot H_2O$

This complex was prepared following the procedure of Basolo et al.[27] The ultraviolet spectrum of the compound in water agreed with that obtained by R. D. Farina.[34] The spectra of this compound was taken in acetophenone at 25°C. Molar absorptivities and their corresponding wavelengths are given below:

Wavelength(Å)	Molar Absorptivity ($M^{-1}cm^{-1}$)
$\lambda_1 = 5500$	90
$\lambda_2 = 4875$	550
$\lambda_3 = 4500$	875

2. Solvent

Acetophenone of various grades was purchased from Eastman and Baker Chemical Companies. The liquid was purified by first freezing out the solvent from other impurities. The melting point of acetophenone is 19°C. During the freeze-separation process, the inside of the beaker was scratched to prevent the solvent from super cooling. Freezing was accomplished in a bucket of ice where the freeze-separation process was repeated twice prior to the distillation. The melt was distilled at reduced pressure as outlined in the literature.[35] The boiling point at 0.2 atm is 55°C for all grades. The first 25cc fraction and the last 50cc fraction of the distillate were discarded with only the middle fraction used in this study.

3. Salts

Reagent grade tetrabutylammonium perchlorate and sodium tetraphenylborate were purchased from Eastman Chemical Company. Lithium tetrafluoroborate was reagent grade and obtained from Matheson, Coleman and Bell Chemical Company.

B. Apparatus

1. Spectral and Kinetics Equipment

The Cary Model 14 recording spectrophotometer was used to follow the rates of reaction and to obtain the spectra measurements. A thermostatable sample jacket, Cary No. 1444100, was mounted in the sample compartment to maintain temperature control inside the spectral cell. Water from a Haake Model FE constant temperature circulator was continuously circulated through the sample jacket via 1/4 inch tygon tubing. The thermostatable cell jacket permits solutions in the spectral cell to be maintained within ±0.03°C at temperatures from -30°C to 55°C.

The temperatures were accurately measured with a laboratory thermometer, Model No. Bat-4, manufactured by Baily Instrument Company, Inc. The laboratory thermometer was equipped with teflon coated thermocouple wires of approximately 0.1 cm in diameter as its sensor. This sensor can be placed in the upper portion of the spectral cell and the cover can be placed on the sample compartment of the Cary 14 which thus allows no interference with either the spectral or kinetics measurements. Since the Haake circulator possesses only a heating element, a cooling source was required for the circulator. This was accomplished by using a bucket of ice water fitted with a vertical centrifugal immersion pump manufactured by the Sargent-Welch Scientific Company. All connections from the pump to the circulator and from the thermo-bath to the circulator were of 1/4 inch Tygon tubing.

Rectangular cuvette cells of 1 cm path length were used for both the spectral and kinetic measurements. Due to the relatively small absorbance changes occurring during the reaction, a more sensitive slide-wire with a 0-0.2 absorption range was used for the kinetics studies, while the slidewire having a 0-2 absorption range was used for most of the spectral measurements. Reactants were delivered to the cuvette by suitable pipettes. They were mixed with a teflon wand which consisted of a plunger with a fitted teflon square in which 1 mm holes were drilled. The plunger was mounted on a glass rod.

2. PDP-8/I Computer

The PDP-8/I computer manufactured by the Digital Equipment Corporation was used to obtain the kinetics results. The program language is "Basic Plus" and consisted of two options:

Option 1 plots the logarithm of absorbance versus time needed to calculate the second order rate constants. Option 0 plots the logarithm of (k/T) versus (1/T) where k is the redox rate constant and T is the temperature. This plot allows the activation parameters to be obtained. The computer program with input instructions is contained in the appendix of this thesis.

3. Distillation Assembly

All components of the distillation assembly were purchased from Corning Glass works. Acetophenone was placed in a single neck 1 liter distilling flask connected to a Kornblum distillation apparatus. Acetophenone was distilled at 0.2 atm pressure with the distillation apparatus connected to a vacuum pump via a distilling head. The vacuum pump manufactured by Precision Scientific Company, Cat. No. 46355, was used with a cold trap consisting of dry ice and isopropyl alcohol. The pressure of the system was measured with a manometer. The heat source of the system consisted of a 1000 ml glas-col heating mantle to which a variable rheostat, Model 3PN116B, Cat. No. 64015 was connected to control the mantle output.

4. Balance

A 160 gm rated Mettler Analytical Balance, Model No. H20T, with an accuracy of ±0.01 mg was used in the weighing of all compounds used in this study. The balance was manufactured by Fisher Scientific Company.

C. Kinetics

Fresh solutions were used for all kinetic runs. The reaction order was first determined at constant ionic strength by varying the concentration of the reactant in excess. The ionic strength was maintained constant by adding appropriate amounts of sodium tetraphenylborate to the solution. The overall reaction order was then obtained by using equal concentrations of each reactant. The concentration of $Co(dipy)_3^{3+}$ was always in sufficient excess (7:1) so that the redox reactions were maintained under pseudo-first-order conditions. This also ensured that all reactions went to completion. All solutions were allowed to reach the specific equilibrium temperature in a thermostated spectral cell prior to each kinetic run. $Co(tripy)_2^{2+}$ was added to the spectral cell to initiate each reaction. The reactions could be followed spectrally since there is an appreciable difference in absorbance between $Co(tripy)_2^{2+}$ and $Co(tripy)_2^{3+}$ at 509 nm, one of the absorption maxima of $Co(tripy)_2^{2+}$. Moreover, at this wavelength, neither $Co(dipy)_3^{3+}$ nor $Co(dipy)_3^{2+}$ interfere with the monitoring of the reaction rate.

Kinetic data were obtained over various ionic strength conditions depending on the solubility of the different salts and the reaction components. The ionic strength ranges were 0.0012-0.0100 M, 0.0012-0.0057 M, and 0.0012-0.0040 M, for tetraphenylborate, tetrafluoroborate, and perchlorate anion solutions respectively. The ionic strength was also varied in the absence of added salts by changing the concentration of reactants to obtain an ionic strength range of 0.0007-0.0027 M. Plots of the logarithm absorbance versus time gave straight lines in every case which is consistent with the pseudo-first-order conditions. The second order rate constant was calculated from the slope of these lines. The plots of absorbance versus time were checked for linearity by hand plotting the data from the Cary 14 prior to use on the computer.

Activation parameters were determined for each anion solution by obtaining rate measurements at temperatures ranging from 25-41°C. Hand plots of logarithm k/T versus 1/T were made to check for linearity. The rate constant and temperature data were then inputted into the computer for determination of the activation parameters, $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$. Details of the computer program are presented in the appendix of this thesis.

Bronsted plots were made in an effort to determine the reactant charges and the degree of ion pairing in the different anion solutions.

D. Equilibrium Study

The equilibrium constant for the redox reaction:

$$\mathrm{Co(tripy)_2^{2+} + Co(dipy)_3^{3+} \rightleftharpoons Co(tripy)_2^{3+} + Co(dipy)_3^{2+}} \qquad (7)$$

in acetophenone was evaluated at 25°C by spectral methods. Equal concentrations of $\mathrm{Co(tripy)_2^{2+}}$ and $\mathrm{Co(dipy)_3^{3+}}$ were mixed and the reaction was followed by observing the disappearance of $\mathrm{Co(tripy)_2^{2+}}$ at 509 nm until there was no further change in absorbance.

The fraction (F) of the reactants converted to products is given by the following equation:

$$F = (A_o - A_f)/(A_o - A_c) \qquad (8)$$

where

A_o = initial absorbance of reactants

A_f = final absorbance of the reaction components

A_c = absorbance of the reaction products assuming the reaction went to completion.

If the activity coefficient of each reaction component is known, the equilibrium constant (K) can be obtained. According to the Debye-Huckel Theory, the activity coefficient is expressed as:

$$-\ln \delta_i = e^3 Z_i^{\,2}(2\pi N_0 \mu)^{1/2}(\varepsilon T)^{-3/2}(1000)^{-1/2} \qquad (9)$$

with all terms having their usual meaning. Since the charges on both the reactants and products are identical, the ratio of the activity coefficients will be unity in the expression for K. Therefore, K can be calculated from the concentration quotient given by the equation:

$$K = (FC_0)^2/(C_0 - FC_0)^2 \qquad (10)$$

where C_0 = initial concentration of each reactant. After simplification, equation (10) can be expressed as:

$$K = F^2/(1 - F)^2 \qquad (11)$$

E. Preliminary Experiments

Early attempts to obtain kinetic data without purification of acetophenone failed. The kinetic results could not be reproduced and the impurities somehow appeared to catalyze the reaction.

The selection of salts in this study was limited by their solubility in acetophenone and by the absence of any interaction with the cobalt complexes. The following salts were insoluble in acetophenone, $(CH_3)_4NBF_4$, $AgBF_4$, $SrBr_2$, $(C_6H_5)_4AsCl$, $Na(NH_4)HPO_4 \cdot 4H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $NaBF_4$. Other soluble salts were inadequate due to their interaction with the reactants causing either dissociation, precipitation or oxidation-reduction of the cobalt complexes. These are: $(CH_3CH_2CH_2)_4NBr$, $(C_4H_9)_4NCl$, $(C_6H_5)_3(C_6H_5{-}CH_2)PCl$, $(C_2H_5)_4NBr$, $\underbrace{CH_2(CH_2)_3}NCSSNH_4$, and LiI with the latter salt giving two reactions. One reaction was too fast to be followed on the Cary 14 while the other reaction believed to be between LiI and $Co(dipy)_3^{3+}$ was followed by the stopped-flow. Additional work is required to gain more insight into this system.

RESULTS AND DISCUSSION

The rate of electron transfer between $Co(tripy)_2^{2+}$ and $Co(dipy)_3^{3+}$ was examined in acetophenone where the reaction was found to be first order in each reactant and second order overall. Pseudo-first-order kinetics was maintained by keeping the oxidant in excess. During the determination of the reaction order, the ionic strength was maintained constant at $\mu = 0.015$ M by introducing the appropriate amount of sodium tetraphenylborate to the solution (see Table I). Linear plots of the logarithm of absorbance versus time confirm the first order dependence with respect to the $Co(dipy)_3^{3+}$ species. Due to the unexpected rapid redox rate in acetophenone where the coulombic repulsion between the similarly charged reactants is assumed to be large because of the relatively low dielectric constant of the solvent, ion pairing was proposed.[36] Therefore, the system was studied in the presence of different anions to examine this effect.

All redox rates were sufficiently slow so that they could be followed on the Cary 14 Recording Spectrophotometer. In order to separate the specific anion effect from the ionic strength influence on this redox system, rate measurements were made in the presence and absence of added salts under similar ionic strength conditions. Table II presents the results of the latter condition over an ionic strength range of 0.0007-0.0027 M. Examination of the results revealed that the rate constant increases with ionic strength in accordance with the Debye-Huckel theory.[37] When the concentrations of the reactants were

TABLE I

DETERMINATION OF THE OXIDANT REACTION ORDER

$t = 25°C$ and $*\mu = 0.015$ M

10^4 Co(dipy)$_3^{3+}$ (M)	10^5 Co(tripy)$_2^{2+}$ (M)	10^2 k_{obs} (sec^{-1})	10^{-1} k (M^{-1} - sec^{-1})
4.36	1.59	2.66	6.1
3.27	1.59	1.99	6.1
2.18	1.59	1.33	6.1
1.09	1.59	0.66	6.1

*Ionic strength was maintained constant using sodium tetraphenylborate.

TABLE II

IONIC STRENGTH EFFECTS ON THE REDOX RATE BETWEEN $Co(dipy)_3^{3+}$ AND $Co(tripy)_2^{2+}$ IN THE ABSENCE OF SALT

t = 25°C

10^4 $Co(dipy)_3^{3+}$ (M)	10^5 $Co(tripy)_2^{2+}$ (M)	10^3 μ (M)	10^{-1} k (M^{-1} - sec^{-1})
4.20	5.90	2.7	8.6
2.10	2.95	1.4	5.7
1.09	1.54	0.7	4.0

held constant and the ionic strength was varied by adding salt to the solution, the rate constant also increased with increasing ionic strength in each salt solution as shown in Tables III-V. Results show that the ClO_4^- and BF_4^- anions used in this study enhanced the rate with respect to the no added salt condition while the $B(C_6H_5)_4^-$ anion lowered it. The order of effectiveness of these anions in influencing the rate of electron exchange is as follows: $ClO_4^- > BF_4^- >> B(C_6H_5)_4^-$. These observations are quite different from that observed in an analogous reaction between $Co(phen)_3^{3+}$ and $Co(tripy)^{2+}$ in water where it was found that nitrate, sulfate and perchlorate had no influence on the redox rate other than a normal ionic strength effect.[34]

The relationship between the rate constant and ionic strength may be represented as:

$$\log k = \log k_0 + 2QZ_1Z_2\mu^{\frac{1}{2}} \Big/ 1 + Ba\mu^{\frac{1}{2}} \qquad (12)$$

where

Z_1Z_2 ≡ reactant charges

k ≡ rate constant at a given ionic strength

k_0 ≡ rate constant at zero ionic strength

μ ≡ ionic strength

a interaction distance of the reactants in the activated complex

Q and B are constants of the solvent defined by equations (13) and (14), respectively:

$$Q = N_0{}^2e^3(2\pi)^{\frac{1}{2}} \Big/ 2.303(10\varepsilon RT)^{3/2}$$

$$B = (8\pi N_0e^2 \Big/ 1000\ \varepsilon kT)^{\frac{1}{2}} \qquad (14)$$

with all terms having their usual meaning. The values of Q and B in acetophenone at 25°C are 4.99 and 69.84 x 10^6 respectively. Crystallo-

TABLE III

EFFECT OF PERCHLORATE ION ON THE REDOX RATE BETWEEN $Co(dipy)_3^{3+}$ AND $Co(tripy)_2^{2+}$

t = 25°C

10^3 ClO_4^- (M)	10^3 *μ (M)	10^{-2} k (M^{-1} - sec^{-1})
3.4	4.1	3.18
2.0	2.7	1.99
1.0	1.7	1.44
0.9	1.4	1.22
0.5	1.2	1.18

*The concentration of $Co(dipy)_3^{3+}$ and $Co(tripy)_2^{2+}$ were 1.09×10^{-4} and 1.54×10^{-5} M, respectively.

TABLE IV

EFFECT OF TETRAFLUOROBORATE ION ON THE REDOX RATE BETWEEN $Co(dipy)_3^{3+}$ AND $Co(tripy)_2^{2+}$

t = 25°C

10^3 BF_4^- (M)	10^3 *μ (M)	10^{-2} k (M^{-1} - sec^{-1})
4.9	5.7	1.90
2.0	2.7	1.32
1.0	1.7	1.12
0.9	1.4	1.07
0.5	1.2	0.78

*The concentration of $Co(dipy)_3^{3+}$ and $Co(tripy)_2^{2+}$ were 1.09×10^{-4} and 1.54×10^{-5} M, respectively.

TABLE V

EFFECT OF TETRAPHENYLBORATE ION ON THE REDOX RATE BETWEEN Co(dipy)$_3^{3+}$ AND Co(tripy)$_2^{2+}$

t = 25°C

10^3 B(C$_6$H$_5$)$_4^-$ (M)	10^3 *μ (M)	10^{-1} k (M^{-1} - sec^{-1})
10.0	10.7	17.0
2.0	2.7	7.7
1.0	1.7	6.1
0.9	1.4	4.8
0.5	1.2	4.6

---

*The concentration of Co(dipy)$_3^{3+}$ and Co(tripy)$_2^{2+}$ were 1.09×10^{-4} and 1.54×10^{-5} M, respectively.

graphic studies[38] on analogous compounds revealed that a is on the order of 11.6 Å. Moreover, kinetic results obtained on a redox reaction in water involving compounds similar to those used in this study were in good agreement with the above value for a.[34] Substitution of the values for Q, B and a in equation (12) results in the following equation applicable at 25°C:

$$\log k = \log k_0 + 9.98\, Z_1Z_2\mu^{\frac{1}{2}} \Big/ 1 + 8.1\mu^{\frac{1}{2}} \qquad (15)$$

Plots of logarithm rate constant vs $\mu^{\frac{1}{2}}/1 + 8.1\mu^{\frac{1}{2}}$ in each solution were linear (Figure 2). The slope of these lines give 9.98 Z_1Z_2 from which the product of the charges on the reactants in each solution can then be obtained. The results are given below:

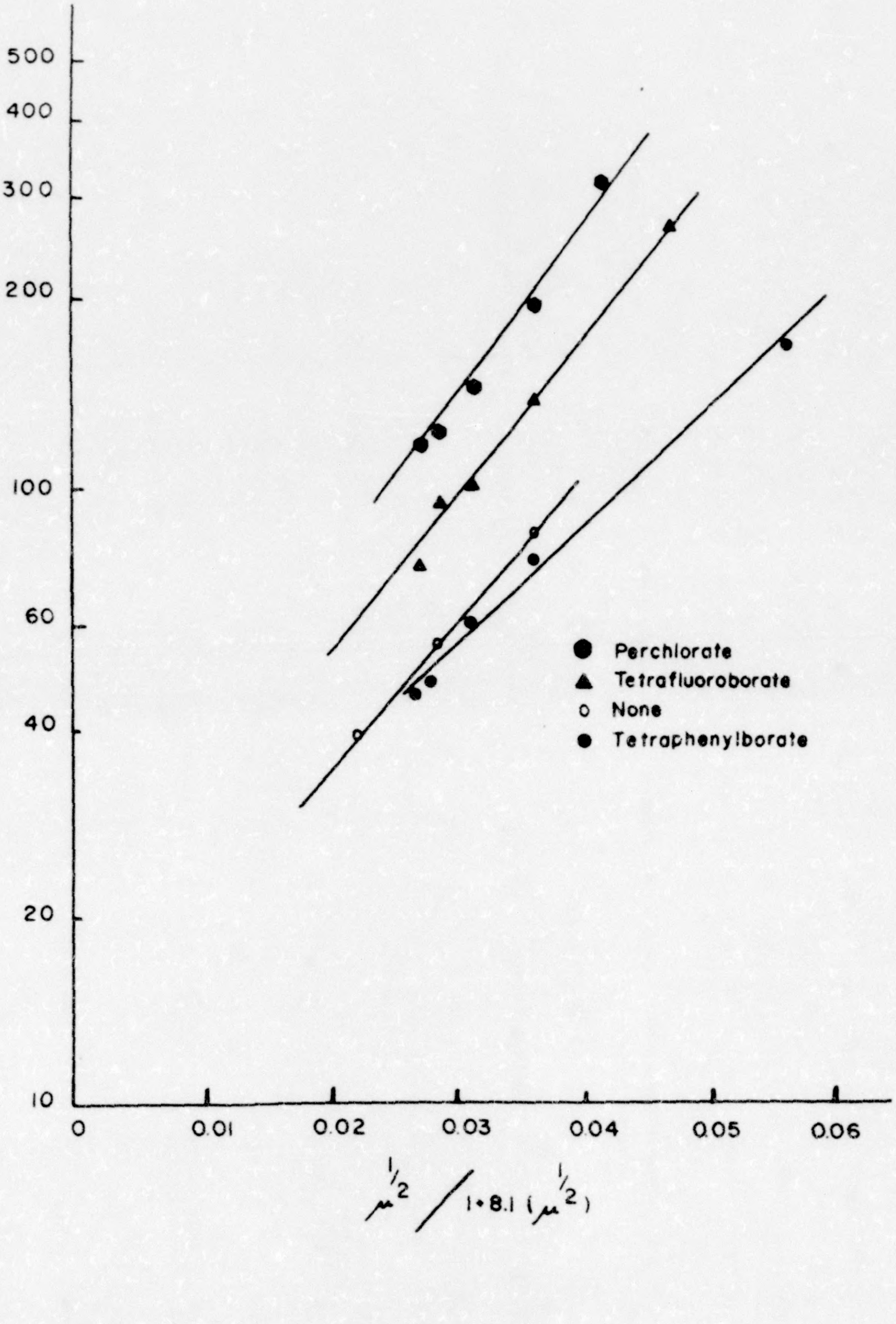
Salt	Z_1Z_2
ClO_4^-	2.9
BF_4^-	2.7
None	2.5
$B(C_6H_5)_4^-$	1.9

Inspection of the product of the reactant charges suggests that the degree of ion pairing decreases as follows:

$$B(C_6H_5)_4^- > \text{none} > BF_4^- > ClO_4^-$$

whereas the reverse trend is observed in their rate constants. The former trend may be simply related to the size of the anion where the large $B(C_6H_5)_4^-$ would tend to promote ion pairing with the large cationic reactants.[39] The latter trend is not too unexpected due to ion pairing which reduces the ionic strength of the solution as well as the product of the reactant charges. Hence, the rate constant will be lower for a given salt concentration as shown in equation (12). These

Figure 2. Plots of Logarithm Rate Constant as a Function of Ionic Strength


500
400
300
200
100
60
40
20
10
k(M⁻¹ – sec⁻¹)
0
0.01
0.02
0.03
0.04
0.05
0.06
μ^½ / 1+8.1 (μ^½)
● Perchlorate
▲ Tetrafluoroborate
○ None
● Tetraphenylborate

results show that in acetophenone, the order of effectiveness of anions in enhancing the rate of outer-sphere redox reactions is directly related to their ion pairing properties. The greater tendency of an anion to ion pair results in a reduced ionic strength of the solution and a lower product of reactant charges. Consequently, the redox rate constant is lower at the same salt concentration as another anion with less tendency to form ion pairs despite the reduced coulombic repulsion between the reactant cations. The specific anion effects of perchlorate and tetrafluoroborate ions on the rate constant at constant ionic strength have been examined. The ionic strength was maintained constant at 0.067 M by adding the appropriate amounts of tetraphenylborate. The results are presented in Tables VI and VII. In the calculation of ionic strength, it was assumed that the reaction components and added salts are completely dissociated. The results show that at constant ionic strength, the rate constant is independent of the concentration of these added anions. The rate constants at $\mu = 0.0067$ M are 318 and 138 for perchlorate and tetrafluoroborate anion solutions respectively. Although the results show that the redox rate is independent of the anion concentration, there is a specific anion effect influencing the reaction rate.

Since the product of the charges on the reactants are 2.9 and 2.7 in the presence of perchlorate and tetrafluoroborate anions respectively, it is believed that the reaction occurs between $Co(dipy)_3^{3+}$ and $Co(tripy)_2X^+$ where $X = ClO_4^-$, BF_4^-. Although electrostatic effects favor ion pair formation with $Co(dipy)_3^{3+}$ rather than with $Co(tripy)_2^{2+}$, the perchlorate and tetrafluoroborate anion may not form an ion pair with $Co(tripy)_2^{2+}$. Instead, these anions may attack the central metal ion when one of the coordinated donor atoms of tripyridine is disengaged.

TABLE VI

DETERMINATION OF REACTION ORDER WITH RESPECT TO THE PERCHLORATE ION

t = 25°C, *$\mu \equiv 0.0067$ M

10^3 $[ClO_4^-]$ (M)	10^3 $[(C_6H_5)_4B^-]$ (M)	10^2 k_{obs} (M^{-1} - sec^{-1})
3.4	2.6	3.46
3.9	2.1	3.55
4.4	1.6	3.46
4.9	1.1	3.41
5.4	0.6	3.47

*The small contribution towards ionic strength from the concentration of the reaction components is also included.

TABLE VII

DETERMINATION OF REACTION ORDER WITH RESPECT TO THE TETRAFLUOROBORATE ION

$t = 25°C$, $*\mu = 0.0067$ M

10^3 $[BF_4^-]$ (M)	10^3 $[(C_6H_5)_4B^-]$ (M)	10^2 k_{obs} (M^{-1} - sec^{-1})
3.4	2.6	1.50
3.9	2.1	1.50
4.4	1.6	1.53
4.9	1.1	1.50
5.4	0.6	1.50

*The small contribution towards ionic strength from the concentrations of the reaction components is also included.

This may be represented by the reaction scheme shown in Figure 3. This reaction scheme can be supported by the fact that $Co(tripy)_2^{2+}$ is substitution labile like $Cr(dipy)_3^{2+}$ where it is proposed that one end of the ligand repeatedly coordinates and then disengages from the metal ion rapidly.[40] The addition of acid which causes the $Co(tripy)_2^{2+}$ to dissociate in acetophenone is consistent with at least one end of the ligand being disengaged from the metal. The mechanism proposed for the acid dissociation of this complex involves the protonation of one of the uncoordinated donor atoms of tripyridine. It appears that the proton can prevent rejoining of the severed Co-N bond in the tripyridine complex by protonating the detached donor atom of tripyridine.[41] Since the rate constant is independent of the anion concentrations, the anation reaction would be complete over the concentration range of ClO_4^- and BF_4^- used. This seems reasonable because the concentration of the anion is at least five times higher than the concentration of $Co(tripy)_2^{2+}$ even with no salt added. Therefore, the following reaction mechanism is proposed:

$$Co(tripy)_2^{2+} + X^- \xrightarrow[\text{rapid}]{k_1} Co(tripy)_2X^+ \qquad (17)$$

$$Co(tripy)_2X^+ + Co(dipy)_3^{3+} \xrightarrow{k_x} \text{Product} \qquad (18)$$

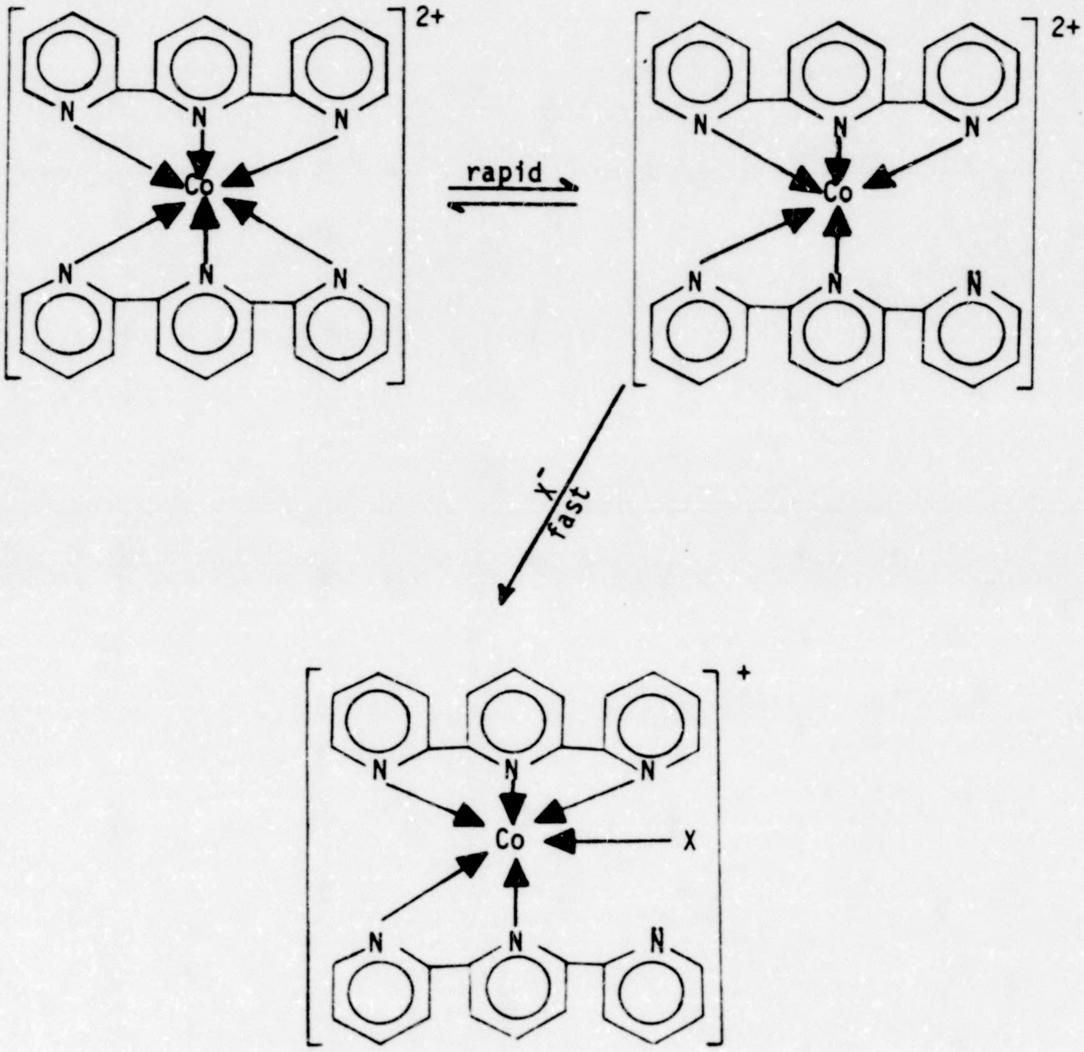
with the rate law being:

$$R = k_x[Co(dipy)_3^{3+}][Co(tripy)_2X^+] \qquad (19)$$

Although the mechanism for perchlorate and tetrafluoroborate is proposed to be the same, the reaction is faster in the presence of perchlorate anion which may be due to the increased ion pairing associated with the BF_4^- anion and its counter ion. An alternate

Figure 3. Mechanism of the Redox Reaction in the Presence of Perchlorate and Tetrafluoroborate Anions

REACTION SCHEME



steric hindrance since both the $Co(dipy)_2^{2+}$ complex and $B(C_6H_5)_4^-$ are bulky. In an effort to determine which of these two mechanisms is operating, attempts were made to obtain the reaction order with respect to the $B(C_6H_5)_4^-$ concentration. All were unsuccessful because in order to maintain constant ionic strength conditions, either perchlorate or tetrafluoroborate was used and both interfered with the reaction even when they were present at low concentration levels.

When no salt is added to the solution, the product of the reactant charges is 2.5. This suggests that two mechanisms are operating simultaneously. The one postulated for BF_4^- and ClO_4^-, and the other proposed for $B(C_6H_5)_4^-$ with the reaction divided between these two mechanisms.

The activation parameters in each salt solution were determined at $\mu = 0.0027$ M over a temperature range of 25-41°C. The results are presented in Table VIII. An error analysis was performed using various combinations of the kinetic data in order to obtain the variation in the rate constants and activation parameters. Evaluations in this manner yielded an experimental error of ±10% for the rate constant, ±1 kcal/mole in $\Delta H^\dagger$ and ±2 eu for $\Delta S^\dagger$. As can be seen from Table VIII, there is no trend between activation parameters and the charges on the reactants. This is not unreasonable since there are many other factors besides those associated with electrostatic effects which influence the activation parameters. The lowest enthalpy of activation was associated with tetraphenylborate where the charges on the reactants are at a minimum. This suggests that electrostatic factors control this activation parameter. However, such is not the case for the perchlorate and tetrafluoroborate anions where the trend is reversed indicating nonelectrostatic factors are more influential. The results in Table VIII

TABLE VIII

SUMMARY OF ACTIVATION PARAMETERS

$t = 25°C$, $\mu = 0.0027$ M

Anion	k_{obs} (M^{-1} - sec^{-1})	$\Delta H^{\dagger}$ kcal/mole	$\Delta S^{\dagger}$ (e.u.)
$B(C_6H_5)_4^-$	77	6.0	-29.2
None	86	8.9	-19.8
BF_4^-	132	12.9	- 5.6
ClO_4^-	199	7.6	-22.7

show that the entropy of activation in each solution is negative. This is consistent with two like charged ionic reactants forming an activated complex of greater charge, which would be expected to be more strongly solvated than both of the separate ions.

The equilibrium constant for the reaction:

$$\mathrm{Co(tripy)_2^{2+} + Co(dipy)_3^{3+} \rightleftharpoons Co(tripy)_2^{3+} + Co(dipy)_3^{2+}}$$

at an ionic strength of 0.002 M and at t = 25°C was found to be 46.4. This value is much greater than those obtained for any other solvent as shown in a previous study.[36] The large value for the equilibrium constant supplies an additional driving force for this reaction in acetophenone and is obviously another important factor which enhances the redox rate.

RECOMMENDATIONS

There are a number of other studies relating to this system which can be performed at a future date. Some possible recommendations are as follows:

1) Study the effect of different cations on the redox rate in acetophenone such as the alkyl ammonium cations of varying chain length.

2) Further investigate the LiI effect on this redox system in acetophenone using the stopped-flow apparatus.

3) Examine this redox system at a relatively high ionic strength where the degree of ion pairing is further promoted.

4) Investigate the salt effect on inner-sphere redox reactions occurring in acetophenone for comparison with redox reactions of the outer-sphere type.

5) Examine salt effects in a mixed solvent system where acetophenone is one of the components.

6) Test the proposed reaction mechanism in the presence of the ClO_4^- and BF_4^- anions using $Co(NH_3)_5Cl^{+2}$ as the oxidant where possible bridging of the chloride group with $Co(tripy)_2^{+2}$ may occur instead of anation.

APPENDIX

COMPUTER PROGRAM

The program consists of a linear least squares curve fit with two options.

Option 0: fit 1/T to log k/T

Option 1: fit T to log A

Input: Option, number of data pairs (M), and data points (k, T) for Option 0, (A, T) for Option 1.

Additional input under Option 1: ionic strength (P1) and concentration of excess reactant (F).

Output: data in form to be plotted, slope.

Additional output dependent upon option.

Option 0: Activation parameters $\Delta H^{\dagger}$ (H) and $\Delta S^{\dagger}$ (S)

Option 1: Second-order rate constant (G)

```
 5 INPUT "OPTION" 0
 7 IF 0=1 THEN 45
 9 PRINT " ACTIVATION PARAMETERS,H* AND S*"
11 INPUT " NUMBER OF DATA PAIRS ",M
13 PRINT " K,T "
15 FOR I=1 TO M
17 INPUT K(I),T(I)
19 C(I)=LOG(K(I)/T(I))
21 V(I)=C(I)
23 W(I)=1/T(I)
25 NEXT I
27 FOR I=1 TO M
29 PRINT "LOG(K/T)=",V(I),"VS","1/T=",W(I)
31 NEXT I
34 GO TO 70
45 PRINT " SECOND ORDER RATE CONSTANTS "
46 INPUT "IONIC STRENGTH ";P1
47 INPUT " NUMBER OF DATA PAIRS ",M," CONCENTRATION ",F
```

```
 49 PRINT " A,T "
 51 FOR I=1 TO M
 53 INPUT K(I),T(I)
 55 C(I)=LOG(K(I))
 57 V(I)=C(I)
 59 W(I)=T(I)
 61 NEXT I
 62 FOR I=1 TO M
 63 PRINT "LOG(A)= ",V(I),"VS","T=",W(I)
 65 NEXT I
 70 L1=1/LOG(10)
 73 N1=1
 75 PRINT
 77 N+N1+1
 80 FOR I=1 TO M
 83 IF ABS(W(I))>0 THEN 87
 85 W(I)=1.E-8
 87 NEXT I
 90 FOR I=1 TO M
 93 FOR J=1 TO N
 96 FOR K=1 TO N
 99 A(K,J)=A(K,J)+W(I)∧(J+K-2)
100 NEXT K
103 B(J)=B(J)+V(I)*W(I)∧(J-1)
106 NEXT J
110 NEXT I
112 PRINT
115 D=A(1,1)*A(2,2)-A(2,1)*A(1,2)
117 IF D=0 THEN 155
119 Y1=(B(1)*A(2,2)-B(2)*A(1,2))/D
121 S-(A(1.1)*B(2)-A(2,1)*B(1)/D
124 PRINT "SLOPE=",S
127 IF 0=1 THEN 145
130 H=S*-1.987
133 P=(C(1)-LOG((1.38E-16)/6.62E-27)+H/(1.987*298))*1.987
135 PRINT "H*=",H,"S*=",P
137 PRINT " H* AND S* ARE THE ACTIVATION PARAMETERS."
140 GO TO 170
145 G=S/-F
147 PRINT " SECOND-ORDER RATE CONSTANT IS EQUAL TO =",G
148 PRINT " IONIC STRENGTH ";P1
150 GO TO 170
155 PRINT " NO SOLUTION."
170 STOP
172 END
```

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