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William Prow
Western Kentucky University

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ELECTRON TRANSFER RATE BETWEEN COBALT(II)-COBALT(III) POLYPYRIDYL COMPLEXES IN NONAQUEOUS SOLVENTS

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Master of Science

by
William F. Prow
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ELECTRON TRANSFER RATE BETWEEN COBALT(II)-COBALT(III) POLYPYRIDYL COMPLEXES IN NONAQUEOUS SOLVENTS

APPROVED August 2, 1973:
(Date)

Robert D. Farina
Director of Thesis

Curtis C. Wilkins

John T. Riley

Elmer Gray
Dean of the Graduate School

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William F. Prow

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STATEMENT OF THE PROBLEM

Numerous studies have been made in recent years on electron transfer reactions of transition metal complexes which proceed by either an inner- or an outer-sphere mechanism. However, except for the Fe(II)/Fe(III) isotopic electron exchange system, few of the studies have been conducted in other than aqueous media. This study was undertaken to examine solvent effects on redox reactions of transition metal complexes which proceed by an outer-sphere mechanism.

During this study, the electron exchange rate between the bis(2,2',2"-tripyridyl)cobalt(II) complex and the tris(2,2'-dipyridyl)cobalt(III) complex was measured in a number of nonaqueous solvents. Rate measurements were made at three or more temperatures in order to determine the activation parameters. The free energy drive for the electron transfer reaction in each solvent was evaluated from the equilibrium constant which was determined by either spectral or kinetic methods. In the case of water, a third method was used to determine the equilibrium constant which involved measurements of the redox couple of each reactant.

The results of this kinetic study are discussed in terms of the theoretical predictions of Marcus.

INTRODUCTION

Electron transfer reactions of transition metal complexes have been of interest for many years. Much work has been done to elucidate and substantiate the mechanisms of electron transfer reactions in solution. These reactions are normally discussed in terms of two principal mechanisms which proceed by either an inner- or outer-sphere path. Detailed reviews on both the "inner-"[1-3] and the "outer-"[4, 5] sphere mechanisms are reported in the literature.

The inner-sphere mechanism involves a bridged activated complex in which an atom or group of atoms is part of the coordination sphere of both reacting partners. The characteristic feature is that the coordination sphere of at least one of the partners has been entered and new bonds are established in forming the activated complex. In properly chosen systems, the new bonds formed will be retained when the metal ions separate to form products.

Proof of the inner-sphere mechanism usually takes the form of product analysis. The investigations of Taube and co-workers[6] on the reactions of pentaamine-Cobalt(III) complexes with Chromium(II), and the isolation of $(NC)_5Co\text{-}NC\text{-}Fe(CN)_5^{6-}$ as a product in the $Fe(CN)_6^{3-}/Co(CN)_5^{3-}$ reaction[7] represent two of the more elegant demonstrations of the inner-sphere mechanism.

In contrast to the inner-sphere mechanism, the outer-sphere mechanism involves only a change in the outer environment of the complex with the inner coordination sphere of both reaction partners remaining intact throughout the reaction. Bonds are neither formed nor cleaved during the reaction. For this reason, the attention of theoreticians has been mainly focused on the outer-sphere type reactions.

Franck-Condon restrictions invoked in the study of absorption and emission of light by molecules are also an important factor in electron transfer reactions occurring by an outer-sphere mechanism. The "electron jump" process involving the transfer of an electron from an orbital belonging essentially to one metal complex to an electronic orbital belonging to the other metal complex occurs in a very short time ($\sim 10^{-15}$ sec) compared to that required for nuclear position changes ($\sim 10^{-13}$ sec). The Franck-Condon principle requires that the nuclear positions remain essentially unchanged during the electronic transition. Therefore, two forms of the activated complex are considered in which both complexes have the same spatial arrangement about the nuclei. One form of the activated complex has the electronic configuration of the reactants while the other has the electronic configuration of the products. These complexes are designated the reactants' activated complex and the products' activated complex respectively.[8a]

A major consequence of the Franck-Condon principle is that the total energy of the reactants' activated complex and that for the products' activated complex must be identical. This electronic degeneracy was recognized by Libby.[9] R. A. Marcus[5, 10-12] has generalized the Franck-Condon restriction for a macroscopic system of many activated complexes and advanced one of the more acceptable theories of outer-sphere redox reactions. In the theory, the activated complex is not an ordinary member of the allowable states of the system as in the absolute rate theory but possesses an equivalent equilibrium electron distribution.

The rate constant is given by

$$k = Z\exp^{-\Delta G^{\dagger}/RT} \qquad (1)$$

where

$Z \equiv$ collision number between uncharged molecules ($\sim 10^{11}$ $M^{-1}sec^{-1}$)

$\Delta G^{\dagger}$ = total energy of activation

and RT has its usual meaning.

According to the Marcus theory, the total energy of activation is composed of the following three parameters:

$$\Delta G^{\dagger} = \Delta G_c^{\dagger} + \Delta G_o^{\dagger} + \Delta G_i^{\dagger} \qquad (2)$$

In this equation, $\Delta G_c^{\dagger}$ represents the total coulombic free energy which is the work required to bring the reactants together in the activated complex. $\Delta G_o^{\dagger}$ and $\Delta G_i^{\dagger}$ are the reorganizational free energies of the solvent and reactants respectively.

The coulombic force between complex ion reactants is repulsive when two ions have the same charge and attractive when the reacting ions are oppositely charged. The $\Delta G_c^{\dagger}$ can be approximated by the Debye-Huckel theory[13] as:

$$\Delta G_c^{\dagger} = \frac{Z_1 Z_2 e^2}{\varepsilon r_{\dagger}} \exp^{-} \left[r_{\dagger} \frac{(8\pi e^2 N o \mu)^{\frac{1}{2}}}{(1000\ \varepsilon\ kT)^{\frac{1}{2}}} \right] \qquad (3)$$

where

Z_1, Z_2 ≡ charge of reactants

e ≡ electronic charge

$r_{\dagger}$ = distance between reactants in the activated complex

ε = dielectric constant of the medium

μ = ionic strength of the medium

k = Boltzman's constant

other quantities not previously defined are π and N_o which have their usual meaning.

For redox reactions of the type examined here, specific information is required about the changes in the metal complex geometry necessary for mixing of electronic states in such a way as to satisfy the Franck-Condon restrictions. The $\Delta G_i^{\dagger}$ considers only the simplest kind of ligand reorganization, i.e., changes in the vibrational coordinates associated with the simple "breathing" motions of the ligands coordinated to the central metal, that are required to produce the degenerate state of the activated complex. The expression obtained by Marcus[10] for the inner-sphere reorganizational energy is:

$$\Delta G_i^{\dagger} = m^2 \lambda_i \qquad (4)$$

where

m ≡ mixing parameter

and λ_i is given by the expression:

$$\lambda_i = \sum_j \frac{fj fj^P}{fj + fj^P} (\Delta r_j^o)^2 \qquad (5)$$

where

f_j, f_j^P ≡ force constants of the jth vibrational coordinate of species participating as a reactant and product respectively

Δr_j° ≡ changes in bond lengths and bond angles in the reactants.

Marcus[11] calculated the free energy required to reorganize the outer solvation sphere of the reactant ions from the equilibrium solvent orientation of the ground state reactants in the collision complex, to a non-equilibrium arrangement. He considered the solvent to be a classical dielectric continuum. The expression obtained for the solvent reorganizational energy is:

$$\Delta G_o^\dagger = m^2 \lambda_o \qquad (6)$$

with λ_o given by:

$$\lambda_o = (\Delta Z)^2 e^2 \left[\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_\dagger}\right]\left[\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right] \qquad (7)$$

where

ΔZ ≡ number of electrons transferred

r_1, r_2 ≡ radii of reactants

$r_\dagger$ ≡ distance between reactants in the activated complex, usually given as the sum of r_1 and r_2

ε_{op} ≡ optical dielectric constant or refractive index squared and all other terms have been previously defined.

The mixing parameter in equations 4 and 6 is given by the expression:

$$m = -\frac{1}{2} - \frac{\Delta G^\circ + (\Delta G_{c,P}^\dagger - \Delta G_{c,R}^\dagger)}{2\lambda} \qquad (8)$$

where

ΔG^{o} ≡ free energy drive of the reaction

$\Delta G^{\dagger}_{c,P}$, $\Delta G^{\dagger}_{c,R}$ ≡ the work terms for products and reactants respectively which can be calculated from equation 3

$$\lambda \equiv \lambda_o + \lambda_i \qquad (9)$$

other terms have been previously defined.

The importance of the solvent to electron transfer reactions was recognized by a number of workers.[9, 14-16] Numerous studies have been made which have centered on the Fe(II)/Fe(III) electron exchange in a variety of solvents. In nitromethane[17] and anhydrous alcohols,[18] the transfer rate is found to be extremely slow. Moreover, in mixed water-alcohol and mixed water-acetone media, there was a decrease in rate with water concentration.[19] All of the earlier results in the Fe(II)/Fe(III) system in the different solvents have been interpreted in terms of an inner-sphere mechanism with water as the required bridging group to allow the transfer of a hydrogen atom.

In DMSO, Menashi et. al.[20] reports a fairly rapid electron transfer rate for the Fe(II)/Fe(III) system. A bridged outer-sphere mechanism involving the S=O entity as a bridging group is proposed. The Fe(II)/Fe(III) exchange in solid ice media[21] is more difficult to explain in terms of an inner- or an outer-sphere mechanism since the Fe^{2+} and Fe^{3+} ions are rigidly held in a lattice. The electron exchange is believed to occur even when the reactants are an average 100 Å apart. An explanation is offered in terms of a Grotthus type mechanism. Since the Arrhenius plot is a continuation of that observed in the liquid phase, it can be argued that a similar mechanism is effective in the liquid phase.

Other systems which have been examined in aqueous mixtures of organic solvents include the $Co(phen)_3^{2+}/Co(phen)_3^{3+}$ isotopic exchange[22] and the reduction of cis-chloro-2-aminoethanolbis(ethylenediamine) cobalt(III) by iron(II).[23] Unusually rapid exchange rates have been observed with the $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$ system,[24, 25] as well as with aromatic anion and cation radicals studied in a variety of nonaqueous solvents.[26]

The bis(2,2',2"-tripyridyl)cobalt(II)/tris(2,2'-dipyridyl)cobalt(III) system has been examined extensively in water and has been found to proceed by an outer-sphere mechanism.[27] At relatively high ionic strength (salt controlled), the rates in water were sufficiently fast to be measured via the stopped flow technique. However, without the added salt, the rate of reaction is sufficiently slow so that conventional methods, more suitable for nonaqueous solvents, can be employed. The absorption spectra of the complexes involved are ideal for following the redox reaction spectrophotometrically.

In this study, the $Co(tripy)_2^{2+}/Co(dipy)_3^{3+}$ system was examined in a variety of nonaqueous solvents. The electron exchange rates were measured with the Cary 14 spectrophotometer and the activation parameters were determined in each of the solvents. The equilibrium constants and all of the other parameters of the Marcus theory were evaluated in each solvent system.

EXPERIMENTAL

This section consists of five parts; materials, apparatus, kinetics, equilibrium measurements and preliminary experiments.

A. Materials

This portion of the experimental section is divided into two parts. The first deals with the Cobalt(II)-Cobalt(III) polypyridyl complexes while the latter deals with the solvents used in the study. All materials were used without further purification unless otherwise noted.

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

The ligands, dipyridine and tripyridine, obtained from the G. F. Smith Chemical Company were reagent grade and further purified by vacuum sublimation in the usual manner.[28, 29] The source of cobalt in this study was reagent grade $CoCl_2 \cdot 6H_2O$ which was procured from the Matheson, Coleman, and Bell Chemical Company.

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

This complex was prepared as described by Burstall and Nyholm.[30] The ultraviolet spectrum of the complex in water agreed with that obtained by Waind and Martin.[31]

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

This compound was prepared using a method outlined by Basolo et. al.[22] The visible spectrum of the complex in water was in agreement with literature results.[32]

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

The compound was prepared in the anhydrous form as outlined by Burstall and Nyholm.[30] The ultraviolet spectrum in water is similar to that reported by Schläfer[33] with regard to peak positions. However, peak intensities are higher than those extrapolated from his ultraviolet spectrum of the $Co(dipy)_3^{3+}$ ion. This may have resulted from the fact that the complex dissociates in water as evidenced by the non-adherence to Beer's law and measurements of its isotopic exchange rate.[34] Maximum molar absorbtivities were obtained by increasing the ligand to metal ratio to 7:1. Absorption maxima at their corresponding wavelengths obtained at 25°C are presented below.

	ε
λ_1 = 305 nm	3.7×10^4 M^{-1} cm^{-1}
λ_2 = 295 nm	3.9×10^4 M^{-1} cm^{-1}
λ_3 = 243 nm	3.6×10^4 M^{-1} cm^{-1}

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

The complex was prepared as described in reference 22. The ultraviolet spectrum of the compound in water is in agreement with previously reported results.[27]

2. Solvents

Acetonitrile, benzonitrile, glycerol, and nitromethane were spectroquality solvents purchased from the Matheson, Coleman, and Bell Chemical Company. Acetic anhydride (Reagent ACS), N-methylformamide (chromatoquality), and sulfolane (technical) were also purchased from the Matheson, Coleman, and Bell Chemical Company. Sulfolane was further purified by distillation at reduced pressure over sodium hydroxide pellets as outlined in reference 35.

Acetone (AR), acetophenone (Baker grade), and nitrobenzene (AR) were purchased from the Baker Chemical Company. Formamide (99+%) and propylene carbonate (technical) were obtained from Eastman Organic Chemicals. Propylene carbonate was distilled at reduced pressures[36] prior to use.

The upper limit for the water content of all the solvents is approximately 0.3 percent. However, in most solvents, this value was reduced by one order of magnitude. This estimate is based on data supplied on solvent labels and solvent descriptions in suppliers' catalogues. A more detailed description of the properties of the solvents is presented in the Results and Discussion section of this thesis.

B. Apparatus

1. Spectral and Kinetic Measurement Assembly

The Cary Model 14 recording spectrophotometer was used to follow the rates of reaction and to obtain spectral measurements. A thermostatable sample jacket, Cary No. 1444100 was mounted in the sample compartment to maintain a constant temperature 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° to 55°C. Since the Haake circulator possesses only a heating capability, a cooling source was provided to the circulator. Generally this was accomplished by using a bucket of ice water fitted with a vertical centrifugal immersion pump manufactured by the Sargent-Welch Scientific Company. For extended periods of operations at low temperatures, a Forma Temp Jr bath and circulator, Model No. 2132, manufactured by the Forma Scientific Company, was used with ethylene glycol as the circulating solvent. All connections from the pump to the circulator and from the thermo-bath to the circulator were made using 1/4 inch tygon tubing.

Cuvette cells of 1 cm path length were used for the visible spectral measurements and kinetic studies. Generally, the ultraviolet spectral measurements were made using quartz cylindrical cells with a 1 mm path length. For the relatively small absorption changes (0.03 - 0.07 absorption units) occurring during the reaction, a slidewire with a 0 - 0.2 absorption range was used for the kinetic studies, while a slidewire having a 0 - 2 absorption range was generally used for the spectral measurements. Reaction mixtures were transferred to the cuvette by suitable pipettes. Mixing was accomplished with a mixer which consisted of a fitted Teflon square drilled with 1 mm holes and mounted on a glass rod.

2. <u>PDP-8/I Computer</u>

The PDP-8/I Computer manufactured by the Digital Equipment Corporation was used to expedite calculations and alleviate errors during the calculations of the kinetic results. A library linear least squares curve fit program was used. The program language was "FOCAL" (Formulating-On-Line-Calculations in Algebraic Language). The library linear least squares curve fit program was modified to include an option for plotting log (k/T) versus (1/T) needed to calculate the activation parameters. At the same time, output modifications were made so that second order rate constants and activation parameters would be included in the output.

This eliminated the need for additional calculations after the slope of the plot is obtained. The computer program with input instructions is contained in the appendix of this thesis. The program was taped and fed into the computer via the reader assembly prior to each use.

3. Distillation Assembly

All components of the distillation assembly were purchased from the Ace Glass Company. The solvent (sulfolane or propylene carbonate) to be distilled was placed in a 250 ml flask. This flask was connected to a distillation column which in turn was connected to a fraction cutter via a water condenser. This allowed different fractions to be collected in the fraction cutter flasks. Both solvents were distilled at reduced pressure by connecting the fraction cutter to a vacuum pump manufactured by Central Scientific Company, Cat. No. 21105-1, via a cold trap (ice-acetone). The vacuum in the system was measured by Virtis's McLeod gauges.

4. Electrode Potential Assembly

The apparatus used to obtain the redox couples of the complexes in water consisted of a Corning, Model 12, Research pH meter used with a platinum sensing electrode and a saturated calomel reference electrode.

C. Kinetics

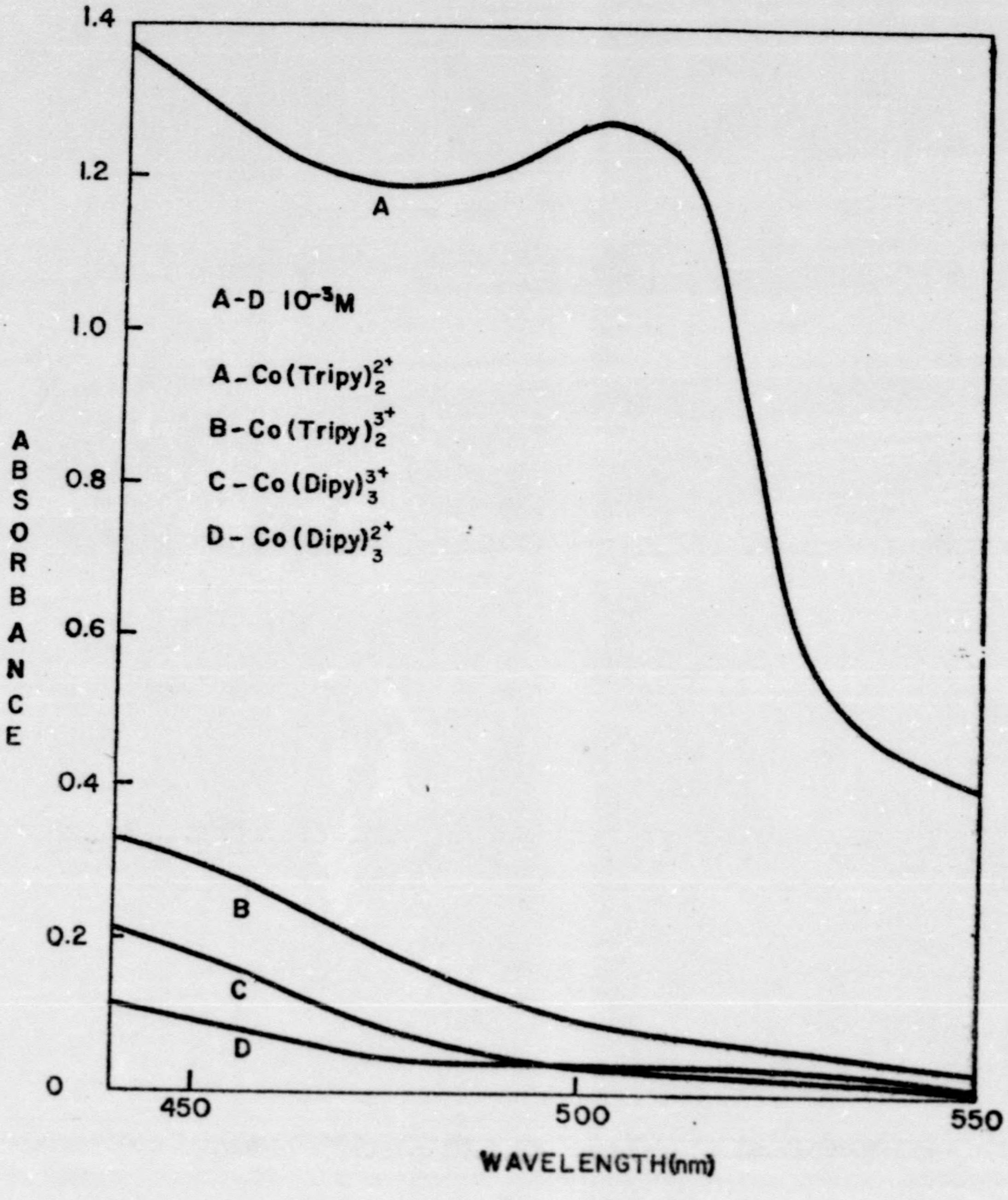
Solutions were freshly prepared prior to all kinetic runs. Pseudo-first-order kinetics were obtained by maintaining the $Co(dipy)_3^{3+}$ in excess. These conditions were used to ensure that the reaction went to completion in all runs. Typically, the $Co(dipy)_3^{3+}$ was maintained in an 8:1 excess over $Co(tripy)_2^{2+}$ in the reaction mixture. The $Co(dipy)_3^{3+}$ was allowed to equilibrate in the thermostated spectral cell to a designated temperature. A small amount of $Co(tripy)_2^{2+}$ ($\leq$ 0.25 ml) was then added and the resulting solution mixed thoroughly. The rate was measured spectrophotometrically by following the disappearance of $Co(tripy)_2^{2+}$ at one of its absorption maxima (505 nm). At 505 nm, none of the other reaction components absorb appreciably as evidenced by the visible spectra of the complexes presented in figure 1. The visible spectra did not vary appreciably in the different solvents.

The ionic strength of a typical reaction mixture was essentially constant in the various solvents and was derived solely from the concentrations of the reaction components. No attempt was made to increase the ionic strength with added salts since the resulting reaction rates would have exceeded the range of the Cary 14 spectrophotometer in most of the solvents.

In every instance, plots of the logarithm of absorbancy versus time gave linear plots. The slopes of the lines yield pseudo-first-order rate constants, from which the second-order rate constants were obtained. The absorbancy and time data from the Cary 14 spectrophotometer were hand plotted to check for linearity prior to feeding the raw data into the computer. The computer values for the rate constants and those obtained from hand calculations were within ±2% for all reactions.

Reactions were run at three or more temperatures over a temperature range of 5° to 50°C and activation parameters were determined. Hand plots of log (k/T) versus 1/T were made to check for linearity. The rate constants and temperature data were then fed into the input of the linear least squares curve fit program 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. An error analysis was

Figure 1. Visible Spectra of Cobalt Polypyridyl Complexes in Propylene Carbonate.


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
ABSORBANCE
450
500
550
WAVELENGTH(nm)
A
B
C
D
A-D 10^{-3}M
A - $Co(Tripy)_2^{2+}$
B - $Co(Tripy)_2^{3+}$
C - $Co(Dipy)_3^{3+}$
D - $Co(Dipy)_3^{2+}$

performed on the computer using different combinations of the kinetic data in order to obtain the variation in the activation parameters. Evaluations in this manner yielded an experimental error in $\Delta H^{\dagger}$ of ±1 kcal/mole and ±2 e.u. for $\Delta S^{\dagger}$.

D. Equilibrium Measurements

Two methods were employed to evaluate the equilibrium constant (K_{eq}) for the reaction in nonaqueous solvents:

$$\mathrm{Co(tripy)_2^{2+} + Co(dipy)_3^{3+} = Co(tripy)_2^{3+} + Co(dipy)_3^{2+}} \qquad (10)$$

The principal method employed for most of the solvents was to evaluate the equilibrium constant by spectrophotometric techniques. In this method, solutions of $\mathrm{Co(tripy)_2^{2+}}$ and $\mathrm{Co(dipy)_3^{3+}}$ were mixed at equal concentrations. All concentrations were checked spectrally against previous spectral measurements and the reactants were equilibrated at 25°C prior to mixing. The equilibrium reactions were generally followed by observing the disappearance of the $\mathrm{Co(tripy)_2^{2+}}$ at 505 nm until no detectable change in absorption occurred.

The fraction (F) of the reactants converted to products was evaluated from the following expression:

$$F = \frac{A_o - A_f}{A_o - A_c} \qquad (11)$$

where

A_o = initial absorbance

A_f = final absorbance

A_c = theoretical absorbance at reaction completion

The K_{eq} can be calculated provided the activity coefficients of each reaction component is known. Based on the Debye-Huckel theory, the expression for the activity coefficient is $-\ln \gamma_i = e^3 Z_i^{\,2} (2\pi N_o \mu)^{\frac{1}{2}} [(\varepsilon kT)^{-\frac{1}{2}}]^3 (1000)^{-\frac{1}{2}}$. Since the charges on both the reactants and products are identical, the ratio of the activity coefficients is unity in the expression for K_{eq}. Therefore, K_{eq} can be readily calculated from the concentration quotient given by the relationship:

$$K_{eq} = \frac{(FC_o)^2}{(C_o - FC_o)^2} \qquad (12)$$

where C_o = initial concentration of each reactant.
Equation 12 can be further simplified to the expression:

$$K_{eq} = \frac{F^2}{(1 - F)^2} \qquad (13)$$

An additional method was employed to determine the equilibrium constant in those solvents where the reverse reaction could be measured. The reverse reaction was conducted under identical conditions to that of the forward reaction. There are problems encountered in this method which have not been solved for most of the solvents. The principal difficulty is one of solubility. The $Co(tripy)_2^{3+}$, oxidant, which must be held in excess for the reverse reaction due to the substitution lability of the reductant, is the least soluble of the reaction complexes. Due to an unfavorable equilibrium, a larger excess reactant is needed if the reaction is to proceed to completion. The solubility prevents the achievement of solutions to the desired levels of concentration. Moreover lowering the concentration of $Co(dipy)_3^{2+}$ to achieve a larger excess of oxidant to reductant causes a decrease in the absorption change of the reaction thus making it difficult to measure. This particular method could only be used with propylene carbonate and water.

A third method was employed to achieve the best possible value for the equilibrium constant of water which is used as the standard solvent for comparing the equilibrium constants and kinetic data. From the redox couples of the reactants, the equilibrium constant can be evaluated from the following relationships:

$$K_{eq} = \exp^{-[\frac{\Delta G^\circ}{RT}]} \qquad (14)$$

where ΔG° can be determined from the expression:

$$\Delta G^\circ = -n\,F\,E^\circ \qquad (15)$$

and

n = number of electrons transferred

F ≡ Faraday (23,070 cal/V)

E° = standard electrode potential difference between the redox couple of each reactant.

The redox couples of the Co(II)/Co(III) tris(dipyridyl) and Co(II)/Co(III) bis(tripyridyl) complexes were measured in water at 25°C using equal concentrations of the complexes. The concentration of each species after mixing was approximately 2.3×10^{-4} M. The accuracy of the method was tested by first measuring the Co(II)/Co(III) tris(dipyridyl) couple whose value has been previously reported.[27] The agreement was excellent.

Deionized and triply distilled water was used to make up the solutions. Purging solutions with dry nitrogen and adding excess ligand showed little effect on the potential.

E. Preliminary Experiments

1. Selection of Solvents

The selection of solvents in this study was limited by the solubility of the complexes and by the absence of solvent-complex interaction as evidenced by Beer's law plots. The complexes were soluble in pyridine, benzaldehyde, and formic acid. However, due to obvious solvent-complex interactions, these solvents could not be used in the study. Solubility prevented the use of benzophenone and propiophenone.

2. Inert Salt Addition

In experiments with acetophenone, an attempt was made to obtain an inert salt which would be soluble in all of the solvents. Since the most difficulty with solubility was encountered with this solvent, it was reasoned that if a salt were soluble in this particular solvent, no difficulty would be encountered in any of the other solvents. Efforts were expended primarily on sodium salts. The salts tested for solubility include NaF, NaCl, NaI, NaCN, $NaNO_3$, $NaO_2C_2H_3$, NaOH, $NaOCH_3$, $NaClO_3$, $NaClO_4$, Na_2SO_4, $NaHSO_4 \cdot H_2O$, $NaNH_4HPO_4$, NaH_2PO_4, Na_2CO_3, $NaHCO_3$, NaO_2CH, $NaSiO_3 \cdot 5H_2O$, $Na_3C_6H_5O_7 \cdot 2H_2O$, NaN_3, and $NaBO_4 \cdot 4H_2O$. Of these salts, only the sodium perchlorate was found to be soluble to desired levels without undesirable interaction with the solvent. Additionally, tetraethylammonium perchlorate was found to be appreciably soluble in this media. Since the complexes are introduced into solution as perchlorate salts, any addition of salts containing the perchlorate ion intensifies an already difficult solubility problem.

3. Reaction Order

An attempt was made to maintain a constant ionic strength by adding inert salts during the testing of the reaction order where the reactant held in excess was varied. In the higher dielectric media, a constant ionic strength was accomplished by increasing the concentration of either reactant to desired levels without the addition of inert salts. However, in the low dielectric solvents, a constant ionic strength could not be maintained for reasons of insolubility of either the reactants or the salt.

Use of $Co(tripy)_2^{2+}$ as the excess reactant has generally resulted in slightly larger rate constants. This can be attributed to two very probable sources. The $Co(dipy)_3^{2+}$ product may dissociate resulting in an attack of the $Co(tripy)_2^{2+}$ complex by the dipyridine ligand. This may be significant at the concentrations of the $Co(tripy)_2^{2+}$ used. Support for this argument results from the lack of linearity in the pseudo-first-order plots when the reductant is the excess reactant in some of the solvents. These plots have shown a slight increase in slope toward the end of the reaction. The argument is reinforced by the observation that the mixing of the Co(II) complexes generally produces a slight decrease in absorption at high concentrations of $Co(tripy)_2^{2+}$ and low concentrations of $Co(dipy)_3^{2+}$. Another possible source of error is in the reading of absorbance data. At high concentrations of $Co(tripy)_2^{2+}$ where absorbance is particularly high, the accurate measurement of a very small optical density change is difficult.

Differences in rate constants resulting from the reactant held in excess have not been sufficient to suspect a change in reaction order in the solvents. Spot checks in those solvents where the ionic strength could be rigorously controlled have shown the reaction to be second-order, first-order in each reactant.

RESULTS AND DISCUSSION

The redox reaction between $Co(tripy)_2^{2+}$ and $Co(dipy)_3^{3+}$ was investigated in several nonaqueous solvents and second-order kinetics was exhibited in all of the solvents. The rate was sufficiently slow in each solvent so that conventional spectrophotometric methods could be used (see experimental section). The ionic strength which was derived solely through the concentration of the reaction components was maintained essentially constant at 0.0027 M.

The rate constants and activation parameters obtained in the various solvents are presented in Table I. The solvents are listed in order of decreasing dielectric constants. Maximum errors in the rate constants were found to be ±10% estimated from several rate measurements made at the same temperature. The fastest rate was observed in acetophenone, the solvent having the lowest dielectric constant. However, there was no general trend found between the rate constants and dielectric constants of the solvents tested.

The lower enthalpies of activation and entropies of activation were observed in those solvents having the larger dielectric constants except in the case of sulfolane. The negative entropies of activation found in all solvents is consistent with two like charged ionic reactants forming an activated complex of greater charge, which would be expected to be strongly solvated so that more solvent molecules might be required than for the separate ions. However, this assumes that the solvent exerts the greatest effect on the entropy of activation.

TABLE I

SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE $Co(Tripy)_2^{2+}$ REDUCTION OF $Co(Dipy)_3^{3+}$ IN VARIOUS SOLVENTS AT 25°C AND $\mu = 0.0027$ M

Solvent	ε_{25}	k (M^{-1} sec^{-1})	$\Delta H^\dagger$ (Kcal/mole)	$\Delta S^\dagger$ (e.u.)	$\Delta G^{\dagger}$* (Kcal/mole)
N-Methylformamide	182.4	11.5	5.3	-36	16.0
Propylene Carbonate	64.4	2.5	6.5	-35	16.9
Sulfolane	43.3**	3.3***	12.2	-15	16.7
Glycerol	42.5	9.2	5.5	-36	16.2
Acetonitrile	37.5	1.0	7.0	-35	17.4
Nitrobenzene	34.8	10.1	8.1	-27	16.1
Benzonitrile	25.2	19.2	8.2	-25	15.7
Acetic Anhydride	20.1	9.1	10.8	-18	16.2
Acetophenone	17.4	126.0	8.6	-20	14.6

*Calculated from Transition-State Theory

**Measured at 30°

***Extrapolated to 25°

Of the nine solvents studied, two are protic solvents, N-methylformamide and glycerol; three are mono-substituted aromatics, nitrobenzene, benzonitrile, and acetophenone; and two are heterocyclic, sulfolane and propylene carbonate. The redox reaction was also examined in acetonitrile and acetone. Table II contains a summary of those properties which are frequently alluded to as influencing the rates of chemical reactions. The data for this table were extracted from reference 37 except for sulfolane[38] and propylene carbonate.[36]

Both dipyridine and tripyridine are multidentate ligands which strongly coordinate to metal ions. For this reason, it is not expected that they would be easily displaced by any of the solvents examined here. The substitution lability of the $Co(dipy)_3^{3+}$, oxidant,[39] and the $Co(tripy)_2^{2+}$, reductant,[40] in water is very low. In addition, spectrophotometric examinations of the reactants showed no significant spectral changes in the various solvents. All this suggests that the inner coordination shells of both complexes remain intact and the mechanism of the electron transfer is believed to be outer-sphere where the Marcus theory is applicable.

According to the Marcus theory, there are three factors cited in the introduction which effect the rate of outer-sphere electron transfer reactions. These are:

1) the free energy drive of the reaction (ΔG^o)
2) the coulombic free energy ($\Delta G_c^{\dagger}$)
3) the reorganization free energies (λ).

The free energy drive of the reaction was determined by measuring the equilibrium constant in each of the solvents. In addition to those solvents listed in Table I, the equilibrium constant was also measured

TABLE II

PHYSICAL PROPERTIES OF THE VARIOUS SOLVENTS AT 25°C

Solvent	ε	n_D	η(cp)	γ(dynes/cm)	ρ(g/ml)
N-Methylformamide	182.4	1.4300	1.65	38.7	0.999
Formamide	109.5	1.4468	3.30	57.9	1.129
Water	78.5	1.3325	0.89	71.8	0.997
Propylene Carbonate	64.4	1.4209	2.53	——	1.198
Sulfolane*	43.3	1.4820	10.29	35.5	1.261
Glycerol	42.5	1.4730	945.00	63.6	1.258
Acetonitrile	37.5	1.3416	0.34	23.5	0.777
Nitromethane	36.2	1.3796	0.61	36.5	1.131
Nitrobenzene	34.8	1.5500	1.90	42.8	1.198
Benzonitrile	25.2	1.5257	1.22	38.7	1.001
Acetone	20.7	1.3560	0.30	22.7	0.784
Acetic Anhydride	20.1	1.3899	0.85	31.9	1.075
Acetophenone	17.4	1.5321	1.62	38.8	1.024

*All properties were measured at 30°

in three other nonaqueous solvents and in water. The rate constants in these four solvents were measured by a co-worker on this study and have been previously reported.[41] The equilibrium constants and free energy drive of the various solvents are presented in Table III. Except for acetophenone, very small differences exist in the free energy drive of the reaction in nonaqueous solvents compared to that in water as evidenced in column 3, of Table III.

In order to evaluate the remaining two factors which contribute to the total activation energy in the Marcus theory, a number of parameters must be known. The parameters can best be discussed by considering individually those expressions which comprise the total activation energy. These expressions become somewhat simplified at zero ionic strength and hence all rate constants were corrected to zero ionic strength utilizing the Debye-Huckel theory[42] in the following manner:

$$\log k = \log k_o + 2Z_1Z_2Q\mu^{\frac{1}{2}} \tag{16}$$

where

Z_1, Z_2 ≡ reactant charges
k ≡ rate constant at a given ionic strength
k_o ≡ rate constant at zero ionic strength
μ ≡ ionic strength

and Q is defined by the equation:

$$Q = \frac{No^2\, e^3\, (2\pi)^{\frac{1}{2}}}{2.303[(\epsilon RT)^{\frac{1}{2}}]^3(1000)^{\frac{1}{2}}} \tag{17}$$

with all terms having their usual meaning.

TABLE III

EQUILIBRIUM CONSTANTS AND FREE ENERGY DRIVE FOR THE $Co(Tripy)_2^{2+}$ REDUCTION OF $Co(Dipy)_3^{3+}$ IN VARIOUS SOLVENTS AT 25°C AND $\mu = 0.002$ M

Solvent	K_{eq}	$-\Delta G°$ (Kcal/mole)	$\Delta G°_{H_2O} - \Delta G°$ (Kcal/mole)
N-Methylformamide	5.9	1.05	0.05
Formamide	3.6	0.76	-0.24
Water	5.4	1.00	——
Propylene Carbonate	3.5	0.74	-0.26
Sulfolane	3.3	0.71	-0.29
Glycerol	6.4	1.10	0.10
Acetonitrile	6.9	1.14	0.14
Nitromethane	6.2	1.08	0.08
Nitrobenzene	4.6	0.91	-0.09
Benzonitrile	5.6	1.02	0.02
Acetone	6.2	1.08	0.08
Acetic Anhydride	6.2	1.08	0.08
Acetophenone	43.0	2.22	1.22

The Debye-Huckel theory should be applicable as the ionic strengths involved in this study were well below the allowable limit of 0.01 M.[43] A summary of the results of these calculations is presented in Table IV. As expected, large reductions in the rate constants were realized in those solvents with relatively low dielectric constants.

The expression for the coulombic free energy contribution given in equation 3 on page 3 is simplified at zero ionic strength to the form:

$$\Delta G_c^{\dagger} = Z_1 Z_2 \, e^2/\varepsilon r_{\dagger} \tag{18}$$

In the above expression, reactant charges are known if no ion pairing is assumed to occur in any of the solvents, and the dielectric constant for each of the solvents is reported in Table II. Only $r_{\dagger}$, the interaction distance of the reactants in the activated complex needs to be determined in each of the solvents in order to evaluate the coulombic free energy. Because of the difficulty in evaluating $r_{\dagger}$ in each solvent, an assumption is made that the $r_{\dagger}$ does not vary appreciably from its value in water. For similar cobalt complexes in water, a value of 12 Å for $r_{\dagger}$ has been obtained.[28] Using this value allows the coulombic free energy in the various solvents to be estimated.

The reorganizational free energy term (λ) is the sum of the inner-sphere (λ_i) and the outer-sphere or solvent reorganizational parameter (λ_o) as given in equation 9. The outer-sphere reorganizational term given in equation 7 is readily calculated using assumptions analogous to those in the calculation of the coulombic free energy. In addition to the interaction distance in the activated complex, an estimate must be given for the values of the reactant radii. The radii are assumed not to vary appreciably in the different solvents and values in water have

TABLE IV

EXPERIMENTAL RATE CONSTANTS ADJUSTED TO
ZERO IONIC STRENGTH AT 25°C

Solvent	k_2 (M^{-1} sec^{-1})	μ ($M \times 10^3$)	Q ($M^{-\frac{1}{2}}$)	**k_o (M^{-1} sec^{-1})
N-Methylformamide	11.5	2.7	0.14	9.35
Formamide	18.5	4.6	0.31	10.35
Water	9.9	2.3	0.51	5.04
Propylene Carbonate	2.5	2.7	0.69	0.93
Sulfolane	3.3*	2.7	1.24	0.56
Glycerol	9.2	2.7	1.28	1.46
Acetonitrile	1.0	2.7	1.54	0.11
Nitromethane	0.7	4.6	1.63	0.03
Nitrobenzene	10.1	2.7	1.73	0.84
Benzonitrile	19.2	2.7	2.80	0.34
Acetone	10.7	2.3	3.77	0.07
Acetic Anhydride	9.1	2.7	3.94	0.03
Acetophenone	126.0	2.7	4.99	0.11

*Extrapolated to 25°C

**$\log k_o = \log k - 2QZ_1Z_2\mu^{\frac{1}{2}}$

been previously reported to be 6 Å in a similar system.[28] The dielectric constant and refractive index for each solvent is listed in Table II. Using these parameters, the outer-sphere reorganizational term was evaluated. The expression for the inner-sphere reorganizational term is given in equation 5 and a knowledge of force constants and bond distances in the various solvents is needed for an evaluation. Since these parameters are unknown and cannot be easily obtained in the different solvents, use of the experimental results to obtain λ is necessary.

Equation 2 can be rewritten in the form:

$$\Delta G^{\dagger} = \Delta G_c^{\dagger} + m^2\lambda \tag{19}$$

The expression for m, equation 8, can be simplified if the charges and interaction distances in the activated complex are assumed identical for the products and reactants of this system. The resulting equation defining m is then simplified to:

$$m = -\frac{1}{2} - \frac{\Delta G^{\circ}}{2\lambda} \tag{20}$$

Substitution for m in equation 19 results in:

$$\Delta G^{\dagger} = \Delta G_c^{\dagger} + \frac{\lambda}{4} + \frac{\Delta G^{\circ}}{2} + \frac{(\Delta G^{\circ})^2}{4\lambda} \tag{21}$$

Inserting the calculated values of $\Delta G^{\dagger}$ and $\Delta G_c^{\dagger}$ as well as the experimental value of ΔG° allows λ to be determined. Since λ and λ_o can be computed for each solvent, λ_i is obtained from their difference. After λ is determined, the value of m can be obtained from which the reorganizational free energies can be evaluated. A summary of the results of these calculations is given in Table V.

TABLE V

KINETIC RESULTS CALCULATED FROM MARCUS EQUATION

Solvent	k_o (M^{-1} sec^{-1})	$\Delta G^{\dagger}$ (Kcal/mole)	ΔG^{o} (Kcal/mole)	$\Delta G_c^{\dagger}$ (Kcal/mole)	m	$m^2\lambda_o$ (Kcal/mole)	$m^2\lambda_1$ (Kcal/mole)
N-Methylformamide	9.35	13.7	-1.05	0.9	0.49	3.2	9.6
Formamide	10.35	13.6	-0.76	1.5	0.49	3.1	9.0
Water	5.04	14.0	-1.00	2.1	0.49	3.6	8.3
Propylene Carbonate	0.93	15.0	-0.74	2.6	0.49	3.2	9.2
Sulfolane	0.56	15.3	-0.71	3.8	0.49	2.9	8.6
Glycerol	1.46	14.8	-1.10	3.9	0.49	2.9	8.0
Acetonitrile	0.11	16.3	-1.14	4.4	0.49	3.5	8.4
Nitromethane	0.03	17.0	-1.08	4.6	0.49	3.3	9.1
Nitrobenzene	0.84	15.1	-0.91	4.8	0.49	2.6	7.7
Benzonitrile	0.34	15.6	-1.02	6.6	0.49	2.5	6.5
Acetone	0.07	16.6	-1.08	8.0	0.49	3.3	5.3
Acetic Anhydride	0.03	17.0	-1.08	8.3	0.49	3.0	5.7
Acetophenone	0.11	16.3	-2.22	9.6	0.46	2.2	4.5

The inner-sphere reorganization energy of this system in water agrees remarkably well with values reported by Sutin[4] (7.8 kcal/mole) for the $Co(phen)_3^{2+}/Co(phen)_3^{3+}$ system and by Stranks (8.0 kcal/mole) for the $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ after corrections are made for Co-N bond distances.[44] The agreement between the results of this study with that of the tris(phenanthroline) and hexaamine systems cited above suggests that the Co-N bond lengths of the Co(II) and Co(III) complexes studied here are very similar.[45]

Examination of equation 21 above will serve to emphasize the role of $\Delta G°$, $\Delta G_c^\dagger$, and λ in affecting the rates of electron transfer reactions as depicted by Marcus. Even with the available values for the free energy of activation components, the influence of a particular parameter on the redox rate is difficult to assess unless the other parameters either remain constant in all of the solvents being compared or are compensated for. As evidenced in Tables III and V, the former is definitely not the case. Therefore, compensations must be made. This can be accomplished by establishing a standard solvent with which all other solvents can be compared. Since the estimates for reactant radii and the interaction distance in the activated complex have been made in water, this solvent was selected as the "standard."

The free energy drive of the reaction is contained in two terms of equation 21. The first term, $(\Delta G°)^2/4\lambda$, is negligible due to the relative magnitudes of $\Delta G°$ and λ except in the case of acetophenone. The largest calculated value of this term is below 0.04 kcal/mole which is less than 1% of the total free energy of activation in all of the solvents. The second term, $\Delta G°/2$ is also small as is the free energy difference between a given solvent and water. All rate constants were corrected for free energy drive differences using water as the standard solvent. This results in an adjusted overall free energy of activation in a respective solvent, and a corrected rate constant at zero ionic strength (k_o^{corr}). The corrected rate constants are presented in column 1 of Table VI. Lower rate constants are obtained for those solvents having a larger free energy drive than water and vice versa for those solvents having free energy drives less than water. The adjusted overall free energy term then reduces to

$$\Delta G^{\dagger}_{corr} = \Delta G^{\dagger}_{c} + \frac{\lambda}{4} + \frac{\Delta G^{\circ}_{H_2O}}{2} \qquad (22)$$

where $\Delta G^{\circ}_{H_2O}/2$ is a constant.

The contribution of the reorganizational free energies (as reflected in the $\lambda/4$ term) can be displayed graphically in a plot of log k_o^{corr} versus the reciprocal of the dielectric constant, $1/\varepsilon$ given in figure 2. The theoretical slope depicted in figure 2 reflects those terms representing the coefficient of $1/\varepsilon$ in the expression:

$$k_o^{corr} = Ze^{-\Delta G^{\dagger}_{corr}/RT} \qquad (23)$$

and

$$\log k_o^{corr} = \log Z - \Delta G^{\dagger}_{corr}/2.3\ RT \qquad (24)$$

or

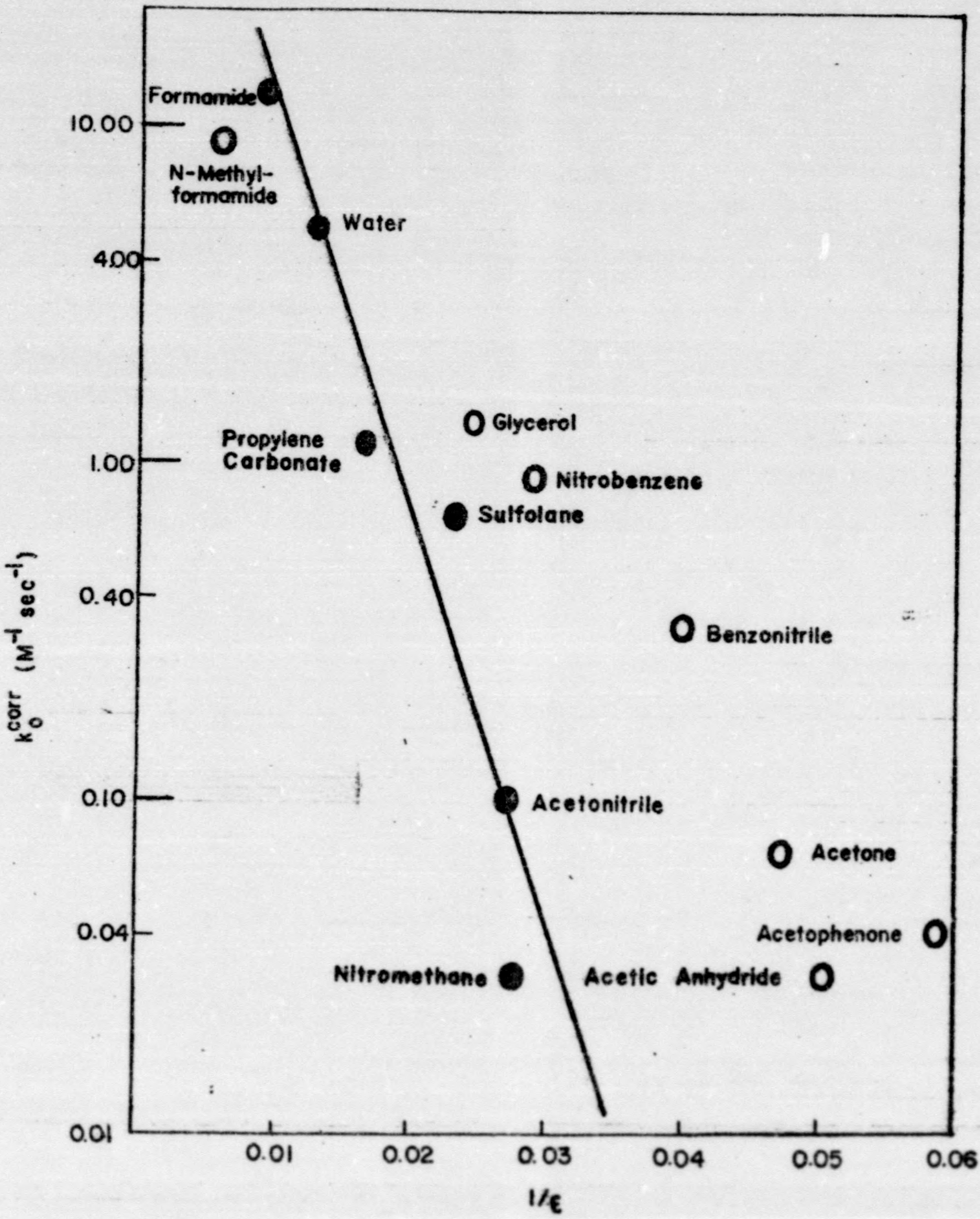
$$\log k_o^{corr} = \log Z - \frac{\Delta G^{\dagger}_{c}}{2.3RT} - \frac{\lambda}{9.2RT} - \frac{\Delta G^{\circ}_{H_2O}}{4.6RT} \qquad (25)$$

TABLE VI

ZERO IONIC STRENGTH RATE CONSTANTS CORRECTED FOR FREE ENERGY DRIVE AS A FUNCTION OF THE RECIPROCAL DIELECTRIC CONSTANT

Solvent	k_o^{corr} (M^{-1} sec^{-1})	ε^{-1}	λ (Kcal/mole)
N-Methylformamide	8.96	.006	53.2
Formamide	12.63	.009	50.0
Water	5.04	.013	49.7
Propylene Carbonate	1.15	.016	51.2
Sulfolane	0.71	.023	47.6
Glycerol	1.35	.024	45.7
Acetonitrile	0.10	.027	49.7
Nitromethane	0.03	.028	51.8
Nitrobenzene	0.91	.029	43.0
Benzonitrile	0.33	.040	38.1
Acetone	0.07	.048	36.3
Acetic Anhydride	0.03	.050	37.0
Acetophenone	0.04	.059	31.0

Figure 2. Effect of Marcus Reorganizational Parameter (λ) on Reaction Rates in the Various Solvents.


Formamide
N-Methyl-formamide
Water
Propylene Carbonate
Glycerol
Nitrobenzene
Sulfolane
Benzonitrile
Acetonitrile
Acetone
Acetophenone
Nitromethane
Acetic Anhydride
10.00
4.00
1.00
0.40
0.10
0.04
0.01
0.01
0.02
0.03
0.04
0.05
0.06
1/ε
k_o^{corr} (M^{-1} sec^{-1})

Substituting $\Delta G_c^{\dagger}$ from equation 18 into equation 25 yields:

$$\log k_o^{corr} = \log Z - \frac{\Delta G^{o}_{H_2O}}{4.6RT} - \frac{Z_1 Z_2 e^2}{2.3RTr_{\dagger}\varepsilon} - \frac{\lambda}{9.2RT} \qquad (26)$$

The slope shown in figure 2 is obtained by assuming values for Z_1, Z_2, and $r_{\dagger}$ of 2, 3, and 12 Å respectively as discussed earlier. Substitution of these values and the appropriate values for R and T yields:

$$\log k_o^{corr} = \log Z - \frac{\Delta G^{o}_{H_2O}}{4.6RT} - \frac{122}{\varepsilon} - \frac{\lambda}{9.2RT} \qquad (27)$$

Inspection of the plot in figure 2 shows that not all solvents lie on a straight line. Since the first two terms (log Z and $\Delta G^{o}_{H_2O}/4.6RT$) are constant, the observed variation in linearity must result from the $\lambda/9.2RT$ term. Provided the previous assumptions are applicable, solvents having reorganizational energies identical to those calculated for water would lie on the theoretical line. The degree of nonlinearity exhibited by a particular solvent simply reflects the difference in their reorganizational energies from those obtained in water.

Figure 2 shows that of the thirteen solvents examined, six were found to have reorganizational energies similar to water. N-methylformamide, whose dielectric constant is larger than water, appears to have reorganizational energies appreciably larger. The six remaining solvents; glycerol, nitrobenzene, benzonitrile, acetone, acetic anhydride, and acetophenone whose dielectric constants are smaller than water seem to have significantly lower reorganizational energies.

As can be seen in Table V, the outer-sphere reorganizational energy of the various solvents did not vary appreciably except in the aromatics where it is significantly lower. This may be attributed to the larger refractive index of these solvents. There is a general decrease in the inner-sphere reorganizational energy when proceeding from solvents of relatively high dielectric constants to solvents of relatively low dielectric constants. This trend is particularly pronounced for solvents of dielectric constants less than 35.

The terms which comprise the inner-sphere reorganizational parameter given in equation 5 are force constants of the metal - ligand bonds of reactants and products, and a term for the change of bond distance and angles (Δr) of the reactants. In solvents of relatively low dielectric constant, an increased electrostatic attraction by the metal for the surrounding ligands is promoted which may reduce the Δr term by decreasing the difference in the radii between the oxidized and reduced forms of the tris(dipyridine) complex. In water, the $Co(dipy)_3^{2+}$ is a high spin complex while the $Co(dipy)_3^{3+}$ is low spin. However, in solvents of relatively low dielectric constant, an increased ligand field results, which in turn could convert the $Co(dipy)_3^{2+}$ to a low spin complex and thus reduce Δr and the inner-sphere reorganizational energy. Although it is expected that the force constants will also be affected in both reactants and products, their ratio may not change significantly. Supporting data for this statement could not be obtained in literature.

The possibility exists that not all of the variation in the $\Delta G_i^\dagger$ term can be attributed to the inner-sphere reorganizational energy. In addition to the terms given by Marcus for $\Delta G^\dagger$, there may be other terms for contributions from hydrogen bonding or other types of bonding between reactants.[8b]

Of the five solvents displaying the greater departure from linearity in figure 2, i.e., where the effect of the reorganization energies appear to be most pronounced, three are aromatics. The other two are acetone and acetic anhydride. Since these solvents do have the lower dielectric constants, the possibility of ion pairing must not be excluded. The probability of ion pairing and the degree to which it occurs would be greater in these solvents than in any of the others. Ion pairing could influence the calculated coulombic free energies which in turn would affect the reorganizational free energies. Since both the reactant charges and their interaction distances are affected, it is difficult to predict the effect of ion pairing on the free energy of activation parameters.

In addition to the explanations offered, there may be a number of other equally probable possibilities.

SUMMARY

The electron exchange reaction between the Co(tripy)$_2^{2+}$ complex and the Co(dipy)$_3^{3+}$ complex was examined in a variety of nonaqueous solvents. Solubility and solvent-complex interaction limited the study to solvents of moderate donor properties with dielectric constants greater than 17. The reaction is believed to proceed by an outer-sphere mechanism in all of the solvents and consequently the Marcus theory is applicable.

Spot checks in a number of solvents indicate that the reaction is second order overall, first order in each reactant. For reactant concentrations in the 10^{-4} - 10^{-3} M range, reaction half-periods of 10 seconds to 40 minutes were obtained. The slowest rate occurred in nitromethane while the fastest rate was measured in acetophenone.

Relatively large negative entropies of activation were observed in all of the solvents. There were no significant differences in the free energy drive of the reaction in the various solvents tested. The spectra of the complexes where measurable, did not vary appreciably in the different solvents.

Based on the predictions of Marcus, the differences in rates for solvents of moderately high dielectric constants (40 - 110) appears to be primarily attributable to coulombic considerations. The outer-sphere reorganizational energies did not vary appreciably for any of the solvents. However, it does appear to be lowest in the aromatic solvents due to their relatively large refractive index. Calculations indicate the inner-sphere reorganizational energy is smaller in solvents of low

dielectric constants than in solvents of relatively high dielectric constant. The similarity in the inner-sphere reorganizational energy of this system in water with those obtained in the $Co(phen)_3^{2+}/Co(phen)_3^{3+}$ and the $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ systems suggest that very little differences exist between the Co-N bond lengths in the Co(II)/Co(III) complexes examined here.

RECOMMENDATIONS

Some possible recommendations for future studies on the electron exchange reaction between the Co(tripy)$_2^{2+}$ complex and the Co(dipy)$_3^{3+}$ complex are as follows:

1) The effect of ionic strength on the rates should be examined in various solvents. Triphenylbenzylphosphonium chloride, which is soluble in aromatic media, would be an excellent salt for this purpose.

2) The effect of water on the redox rate in nonaqueous solvents should be examined by subjecting the solvents to rigorous purification and storage while using anhydrous reactant salts. An alternative would be the intentional addition of water.

3) The effect of oxygen on the system should be examined by conducting the reaction in a nitrogen environment.

4) The effect of mixed solvents on the electron exchange rate of the system should be investigated. Mixtures of solvents with similar donor properties would be of particular interest.

5) Additional solvents with different dielectric constants and donor properties should be tested. Examples are N-methylacetamide, N-methylpropionamide, N,N-dimethylacetamide, benzoyl chloride, selenium oxychloride, benzyl cyanide, ethylene sulphite, iso-butyronitrile, n-butyronitrile, propionitrile, phenylphosphonic difluoride, phenylphosphonic dichloride, and trimethyl phosphate.

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APPENDIX

COMPUTER PROGRAM

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

Option 1: fit X to Log Y.

Option 2: fit 1/X·to Log (Y/X).

Input: option, number of data points (M), and data points (X and Y).

Additional input under option 1: concentration of excess reactant (CN).

Output: data in form to be plotted, coefficients of normal equation, slope, X-intercept, and Y-intercept.

Additional output dependent upon option:

Option 1: second-order rate constant (RK).

Option 2: activation parameters $\Delta H^{\dagger}$(H*) and $\Delta S^{\dagger}$(S*).

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02.05 A !,?OPTION ?,!;S LT=1/FLOG(10)
02.10 A ?M ?,!;S N1=1;T %5,!!"  X       Y"!!
02.20 F L=1,M;A U(L),"    ",V(L),!
02.21 IF (1-OP)2.24;A ?CN? !
02.22 T !" X  LOGY"!;F L=1,M;S V(L)=LT*FLOG(V(L));D 5
02.23 G 2.3
02.24 T !," 1/X  LOG(Y/X)",!
02.25 F L=1,M;S V(L)=LT*FLOG[V(L)/U(L)];S U(L)=1/U(L);D 5
02.30 S N=N1+1;F  I=1,N;S B(I)=0;F J=1,N;S A(I+J*N)=0
02.40 F I=1,M;D 3
02.44 F I=1,M;F J=1,N;D 2.46;S B(J)=B(J)+V(I)*U(I)↑(J-1)
02.45 G 2.5
02.46 F K=1,N;S A(J+K*N)=A(J+K*N)+U(I)↑(J+K-2)
02.48 F J=1,N;T %8.03,A(I+J*N)
02.50 F I=1,N;D 2.48;T B(I),!
02.56 G 4.1
```

```
03.10 I (FABS[U(I)])3.2,3.2;R
03.20 S U(I)=1.E-12

04.10 S D=A(3)*A(6)-A(4)*A(5);I (D)4.2,4.15,4.2
04.15 T !"NO SOLUTION"!;Q
04.20 S YB=(B[1]*A[6]-B[2]*A[5])/D
04.30 S SL=(A[3]*B[2]-A[4]*B[1])/D
04.50 T %10.05,!,?SLOPE?,!,?YB?,!,?1/YB?,!"XA",-YB/SL,!
04.60 I (OP-1)4.62,4.62;T %5.03,"H*", -SL4.576,!
04.61 T "S*",(YB-10.3189)*4.576,!;Q
04.62 T %5.03,"RK",-SL*2.303/CN,!;Q

05.10 T %10.06,U(L),V(L),!
```