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# THE KINETICS OF DISSOCIATION OF FIVE-COORDINATE TRANSITION METAL COMPLEXES IN NONAQUEOUS AND MIXED MEDIA

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THE KINETICS OF DISSOCIATION OF FIVE-COORDINATE TRANSITION  
METAL COMPLEXES IN NONAQUEOUS AND MIXED MEDIA

*University of New Hampshire*

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THE KINETICS OF DISSOCIATION OF FIVE-COORDINATE  
TRANSITION METAL COMPLEXES IN NONAQUEOUS  
AND MIXED MEDIA

BY

Nancy Lou Gottke  
B.S., Georgetown University, 1975

DISSERTATION

Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of

Doctor of Philosophy  
in  
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December, 1980

This dissertation has been examined and approved.

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## ABSTRACT

### THE KINETICS OF DISSOCIATION OF FIVE-COORDINATE TRANSITION METAL COMPLEXES IN NONAQUEOUS AND MIXED MEDIA

by

Nancy Lou Gottke

University of New Hampshire, December, 1980

Five-coordinate complexes of nickel (II), cobalt (II), and copper (II), were prepared from the quadridentate ligand tris-(2-dimethylaminoethyl)-amine, a ligand which forms high-spin trigonal bipyramidal complexes. Previous studies of the dissociation of these complexes in aqueous perchloric acid revealed a single step kinetic process.

Dissociation of the cobalt (II) complex was undertaken in acetonitrile, in dimethyl sulfoxide, and in N,N-dimethylformamide, with monochloroacetic acid as the dissociating agent. Multi-step kinetic behavior was observed. The rate-determining step was considerably faster in dimethyl sulfoxide and in N,N-dimethylformamide than in acetonitrile and in water. Possible mechanisms for the dissociation reaction are described and discussed in terms of solvent properties and crystal field energetics.

Further studies were undertaken in mixed solvents such

as dimethyl sulfoxide/water and N,N-dimethylformamide/water mixtures, to determine the effect of the presence of water on the mechanism of the dissociation reaction.

Kinetic measurements were obtained with a Durrum-Gibson stopped-flow spectrophotometer.

## INTRODUCTION

The structural, spectroscopic, and thermodynamic aspects of five-coordinate complexes of the bivalent first-row transition-metal ions with multidentate amine ligands have been subjected to considerable study in the past fifteen years (Ciampolini and Nardi, 1966; Ciampolini and Speroni, 1966; Paoletti and Ciampolini, 1967; Ciampolini, 1969; Orioli, 1971). Only limited information on the kinetic characteristics of these complexes is available, and the majority of studies were carried out in aqueous systems (West and Lincoln, 1973, 1974; Lincoln and Hubbard, 1974).

The research project which forms the basis of this dissertation involves the dissociation of [tris-(2-dimethylaminoethyl)-amine- $N,N',N'',N'''$ ] -cobalt (II) by monochloroacetic acid in nonaqueous solvents and in binary solvent mixtures of the nonaqueous solvents with water. The information gained from these studies is used to make predictions about the mechanism by which dissociation takes place, the transition state through which the activated complex must pass, and the energetics of the reaction.

Transition state theory is based on the supposition that potential energy of the interacting molecules at the time of collision is known as a function of the relative positions of the various nuclei involved in the reaction

(Frost and Pearson, 1961). There will be a configuration of nuclei of minimum potential energy, related to the activation energy, through which the system is expected to pass in going from reactants to products. This region of configuration space is called the transition state; a system in this region is referred to as an activated complex. The rate of the reaction is assumed to be governed by the rate of passage of the system through the transition state.

Activation parameters for the system may be defined as follows:

$$\Delta G^\ddagger = -RT \ln K^\ddagger \quad (1)$$

$$\Delta H^\ddagger = RT^2 \frac{d \ln K^\ddagger}{dT} \quad (2)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} \quad (3)$$

where  $K^\ddagger$  is similar to an equilibrium constant and  $T$  is the absolute temperature.

Thus, it follows from these definitions that

$$K^\ddagger = e^{-\Delta G^\ddagger/RT} = e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S^\ddagger/R} \quad (4)$$

and the rate constant  $k_r$  may be written

$$k_r = (kT/h) \cdot e^{-\Delta G^\ddagger/RT} \quad (5)$$

where  $k$  is Boltzmann's constant and  $h$  is Planck's constant.

The Arrhenius, or empirical activation energy is defined as

$$\frac{d \ln k_r}{dT} = \frac{E_a}{RT^2} \quad (6)$$

and therefore it follows that

$$\Delta H^\ddagger = E_a - RT \quad (7)$$



for a reaction in solution. If  $E_a$ , the Arrhenius activation energy, is a constant with respect to temperature, then integration of equation (6) results in

$$\ln k_r = -E_a/RT + \text{constant} \quad (8)$$

or

$$k_r = Ae^{-E_a/RT} \quad (9)$$

Thus a plot of the logarithm of the rate constant as a function of inverse temperature will yield a straight line with slope  $-E_a/R$  and intercept  $\ln A$ . An example of an Arrhenius plot is shown in Figure 1-1.

The entropy of activation can be calculated from rate data using the above equations. For a bimolecular reaction, the value of  $\Delta S^\ddagger$  can be correlated with the pre-exponential Arrhenius factor  $A$  in equation (9). In a series of similar reactions, the more negative  $\Delta S^\ddagger$  corresponds to the smaller pre-exponential factor. The experimental value of  $\Delta S^\ddagger$  provides one of the best indications of the nature of the transition state (Moore, 1972). A positive activation entropy means that the entropy of the complex is greater than the entropy of the reactants, that is, the transition state is more disordered than the ground state. For example, a loosely bound complex has a higher entropy than a tightly bound one.

More likely in bimolecular reactions is a decrease in entropy in the transition state. The activated complex is formed by association of two molecules, resulting in a loss of translational and rotational freedom, so that  $\Delta S^\ddagger$  is usually negative.

Figure 1-1. Plot of the natural logarithm of the observed rate constant versus inverse temperature to determine whether Arrhenius behavior is observed.

Reaction of  $\text{Co}(\text{Me}_6\text{tren})^{2+}$  with chloroacetic acid in dimethylformamide.

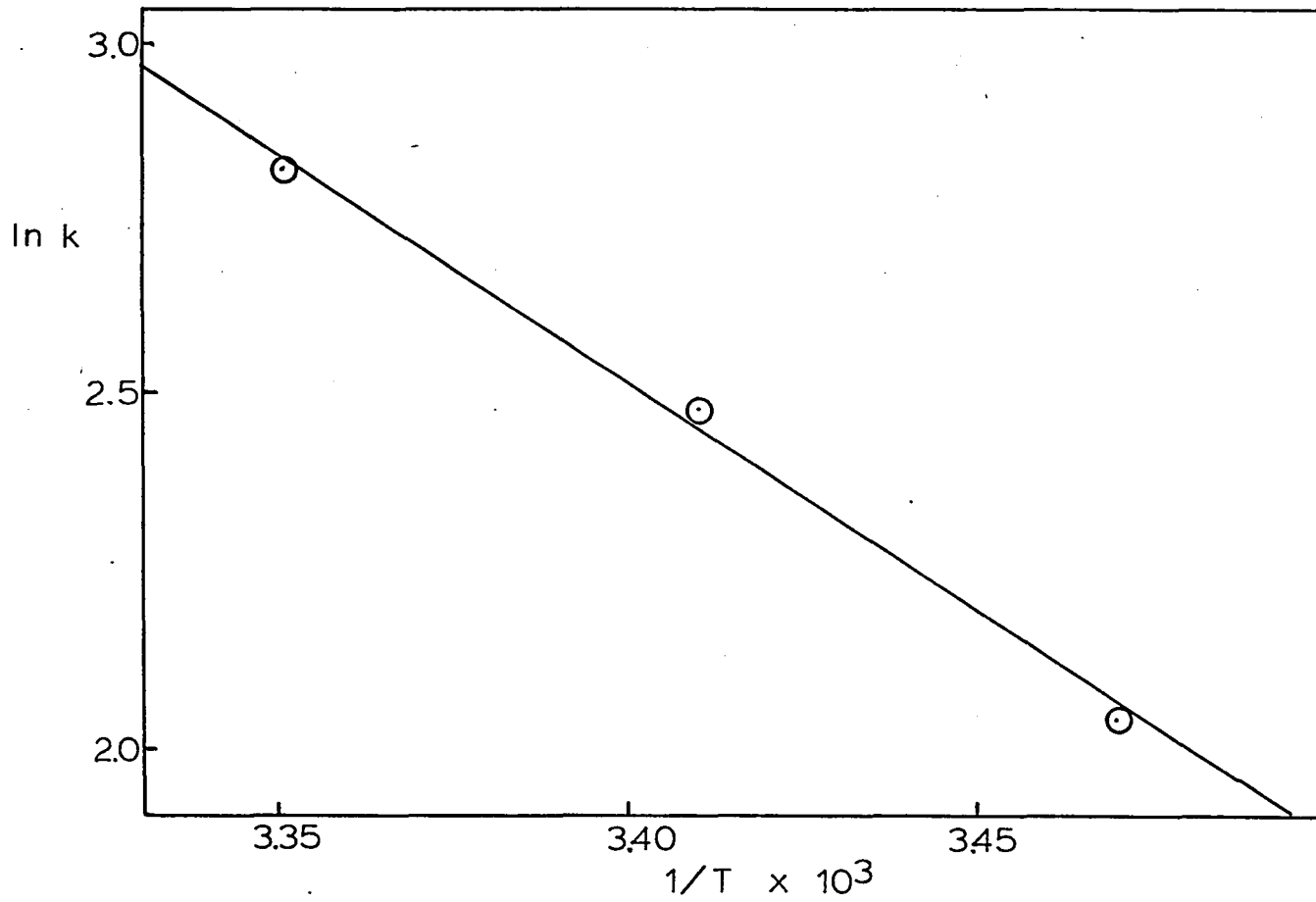


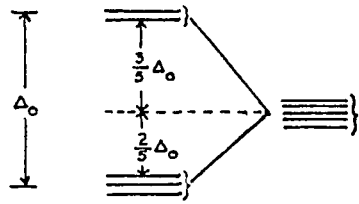
Figure 1-1.

Crystal field theory postulates that the five unoccupied outer-shell d orbitals of a metal ion in the absence of other forces are degenerate. In the presence of an electrostatic field such as that created by ligands, these d orbitals become differentiated. Those orbitals lying in the direction of the ligand(s) are raised in energy relative to the free ion, while those orbitals lying away from the ligand(s) are lowered in energy relative to the free ion. Preferential filling of the low-lying d orbitals causes stabilization of the molecule as compared to random filling. This gain in bonding energy is the crystal field stabilization energy. Metals which can have considerable crystal field stabilization will react preferentially with strong field ligands, which cause large splitting between the higher and lower energy orbitals. Transition metals therefore bond preferentially to nitrogen-containing ligands such as amines, compared to oxygen-containing ligands such as water.

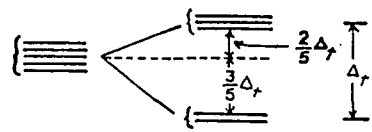
The metals studied in this research project are the first-row transition metals cobalt (II), nickel (II), and copper (II). All have ground state configurations  $3d^n4s^2$ . These metals behave similarly in a trigonal bipyramidal ligand field. The orbital splitting is such that the  $d_{xz}$  and  $d_{yz}$  orbitals are stabilized relative to the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals by an amount  $\delta_1$ ; the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals are stabilized relative to the  $d_{z^2}$  orbital by an amount  $\delta_2$ . For ions of configuration  $d^5-d^8$ , complexes may have either high-spin or low-spin configurations depending on whether

$\delta_2$  is smaller than or greater than the mean spin-pairing energy. Energy diagrams for octahedral, trigonal bipyramidal, and tetrahedral ligand fields are presented in Figure 1-2.

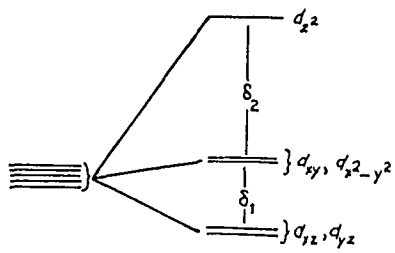
Figure 1-2. Energy diagrams for d orbital splittings due to an octahedral ligand field, a trigonal bipyramidal ligand field, and a tetrahedral ligand field.



Octahedral complex



Tetrahedral complex

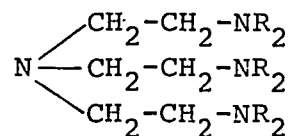


Trigonal-bipyramidal complex

Figure 1-2.

## I. BACKGROUND

One of the most active areas of research in structural chemistry in recent years has concerned five-coordination. Five-coordinate complexes are found for all of the first-row transition metals, from titanium to zinc, and occur about as frequently as square planar or tetrahedral four-coordinate complexes. There is often a real competition between five- and six-coordination, because six-coordinate complexes are almost always favored by transition metal ions relative to complexes of lower coordination number. The subject of this dissertation is high-spin five-coordinate complexes formed with tripod ligands of the type



where R may be hydrogen (tris-(aminoethyl)-amine, or tren), a methyl group (tris-(N,N-dimethylaminoethyl)-amine, or Me<sub>6</sub>tren), or an ethyl group (tris-(N,N-diethylaminoethyl)-amine, or Et<sub>6</sub>tren). These tripod ligands are well adapted to form trigonal bipyramidal complexes, particularly with first-row transition metals such as nickel (II), iron (II), and cobalt (II). Because all the ligands of this family possess identical ethylenic chains, differences in coordination properties are



dependent upon such factors as the effect of the bulkiness or the nucleophilicity of the substituent R groups on the donor groups.

The ligand  $\text{Me}_6\text{tren}$  forms five-coordinate complexes with all the bivalent 3d ions, whereas the unsubstituted ligand  $\text{tren}$  forms either five- or six-coordinate complexes with these ions according to their preference for a specific stereochemistry (Paoletti and Ciampolini, 1967). The effect of increasing the bulkiness of the R groups is to force these ions into five-coordinate geometries. A further increase in the size of the donor groups, as in the ligand  $\text{Et}_6\text{tren}$ , does not appreciably change the trigonal bipyramidal structure of the complexes (Sacconi and Morassi, 1969).

Characterization of Five-Coordinate Complexes. The crystal structure of these complexes has been extensively studied (for example, Ciampolini and Speroni, 1966). The four donor nitrogens of the ligand occupy the three equatorial positions and one axial position of a trigonal bipyramid. The other axial position is filled by a counter ion such as a halide, nitrate, or perchlorate ion. In solution, the counter ion is replaced by a solvent molecule in the inner sphere.

Magnetic moments have been determined for the complexes (Ciampolini and Nardi, 1966). The compounds are all of the high-spin type both as solids and in solution. Conductivity studies in a non-associating solvent such as nitromethane show that the complexes behave as uni-univalent electrolytes;

six-coordinate complexes, having both counter ions in the inner sphere, would be expected to behave as if electrically neutral.

Conclusive evidence concerning the stereochemistry of these complexes is obtained by comparing their electronic spectra with those typical of other high-spin configurations. The spectra of the complexes are characterized by extinction coefficients far greater than those of corresponding six-coordinate complexes. For example, in aqueous solution the  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  ion shows an absorbance maximum at 470 nm with an extinction coefficient of about  $100 \text{ M}^{-1}\text{cm}^{-1}$ ; by comparison,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  has an extinction coefficient of less than  $10 \text{ M}^{-1}\text{cm}^{-1}$ .

Recently, a five-coordinate complex of palladium (II) with  $\text{Me}_6\text{tren}$  was reported (Senoff, 1978), in which proton NMR was used to differentiate between the five- and six-coordinate complexes which had been synthesized under different reaction conditions. The NMR spectrum obtained is characterized by a sharp singlet methyl resonance at 2.6 ppm in  $\text{D}_2\text{O}$ , consistent with the presence of six magnetically equivalent methyl groups. Combined with conductivity measurements and elemental analysis data, this is taken as evidence for the formation of a five-coordinate palladium (II) complex.

Dissociation of Five-Coordinate Complexes. Reactions involving the dissociation of five-coordinate complexes by aqueous acid solutions have been studied, and some results

are described in detail later. In contrast to many six-coordinate complexes, the dissociation of five-coordinate complexes is extremely rapid and must be monitored by techniques such as stopped-flow spectrophotometry or rapid-scan spectrometry.

The order of lability exhibited for dissociation of  $\text{Me}_6\text{tren}$  complexes by aqueous perchloric acid ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ) contrasts with that observed in six-coordinate systems ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ); similar variations in activation enthalpies ( $\Delta H^\ddagger$ ) were also observed (Lincoln and Hubbard, 1974). It is of interest to note that in these studies copper (II) was most labile but also possessed the greatest activation enthalpy.

#### Solvent Exchange Reactions of Five-Coordinate Complexes.

Exchange of acetonitrile on complexes of nickel (II) and cobalt (II) with tren and  $\text{Me}_6\text{tren}$  has been studied by  $^{14}\text{N}$  NMR spectroscopy (West and Lincoln, 1973). The complex  $[\text{Ni}(\text{tren})(\text{CH}_3\text{CN})_2]^{2+}$  is six-coordinate; two exchange rates were observed corresponding to non-equivalent sites on the molecule. The cis- $\text{CH}_3\text{CN}$  ligand may have a longer nickel-nitrogen bond length and thus be more labile than trans- $\text{CH}_3\text{CN}$ . The kinetic parameters indicate considerable lability of coordinated acetonitrile in this position relative to the hexa-solvated species  $[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$ . The results for the five-coordinate complex  $[\text{Co}(\text{tren})(\text{CH}_3\text{CN})]^{2+}$  are consistent with rapid exchange of acetonitrile with the bulk solvent. As a consequence, only a lower limit was set for the observed rate constant for the exchange at 298 K.

In addition to the labilization of coordinated solvent by the polydentate amine ligands, an apparent reduction of lability by  $\text{Me}_6\text{tren}$  was also observed. It is postulated that exclusive five-coordination suggests reduced flexibility relative to the tren complexes, which may preclude significant expansion or geometric rearrangement in the transition state. The relatively inflexible  $\text{Me}_6\text{tren}$  ligand prevents the solvent molecule from approaching close to the metal ion; reduction in solvent assistance drastically reduces lability.

High-pressure NMR has also been used to investigate non-aqueous solvent exchange (Meyer et al., 1979a,b; Newman et al., 1979). Studies of the effect of pressure on six-coordinate metal complexes show that the exchange of dimethylformamide, acetonitrile, and methanol on nickel (II) and cobalt (II) proceeds via a dissociative interchange mechanism, but cobalt (II) exhibits less dissociative character than nickel (II). Evidence based on activation volumes seems to indicate that an associative-dissociative mechanistic changeover may occur in substitution reactions of octahedral complexes.

Relative labilities of five-coordinate nickel (II) and cobalt (II) complexes toward associative solvent exchange have been studied (Curzon et al., 1980). For acetonitrile exchange  $\Delta S^\ddagger$  values were found to be large and negative, and  $\Delta H^\ddagger$  values were found to be low for both the nickel (II) and cobalt (II) complexes. This is in line with an associative interchange mechanism. Previous studies (Herron and Moore, 1979) had shown that six-coordinate complexes exchange via

a dissociative interchange mechanism. The transition state for the associative interchange is thought to have cis-octahedral geometry. Steric hindrance is important in this process, because the site of attack is flanked by the N-methyl groups of the ligand, and approach of the solvent molecule is thereby hindered. The relative labilities of these five-coordinate ions ( $\text{Co}^{2+}$  &  $\text{Ni}^{2+}$ ) is again opposite behavior to that found in octahedral complexes, and arises primarily from the more negative  $\Delta S^\ddagger$  values observed for cobalt (II). This would suggest that there is greater steric hindrance to the approach of incoming solvent for the cobalt (II) complex, which is readily explained if cobalt (II) is less accessible than nickel (II) during formation of the activated complex.

Ligand Exchange at Five-Coordinate Centers. High-spin five-coordinate 18-electron nickel (II) complexes were prepared by adduct formation between a square-planar nickel (II) complex and 2,9-dimethyl-1,10-phenanthroline (Hynes and Brannick, 1977). The nickel (II) complex formed is a five-coordinate square pyramid. The complex was allowed to react with 1,10-phenanthroline and 2,2'-bipyridine. The kinetic data obtained were consistent with an associative mechanism, which produced a 20-electron six-coordinate intermediate involving no change in spin state.

Similar results have been reported for low-spin 18-electron trigonal bipyramidal complexes (Meier et al., 1979); however, Sweigart concludes (1976) that ligand substitution at five-coordinate 18-electron centers will always be

dissociative. When fewer than 18 electrons surround the metal, as with five-coordinate cobalt (II) complexes, associative pathways are expected to be found as well.

Solvating Properties of Solvents. There is no single solvent property which uniquely determines the ability to solvate ions. Some properties which have been invoked to explain a solvent's solvating power include the dielectric constant, the ability of the solvent molecule to donate an electron pair, the Lewis acidity of the ion to be solvated, the extent of solvent structure, and dispersion forces and hydrogen bonding interactions between ion and solvent (Burgess, 1978). Quantitative characterization of a solvent's solvating ability in terms of any of these intrinsic properties has proven to be impossible; these abilities are better expressed in terms of a variety of manifestations of solvent-solute interaction. For example, the  $E_T$  parameter is based on intramolecular charge transfer; solvent Y values are based on the rates of solvolysis of tert-butyl chloride; the Z value scale is based on charge-transfer frequencies for 1-ethyl-4-carbomethoxypyridinium iodide. The most clearly related parameter is Gutmann's donor number, which will be discussed more extensively later. This is a reflection of the ease of donation of the solvent molecule's lone pair.

Solvent Effects on the Dissociation of Six-Coordinate Complexes. Rate constants and associated activation para-

meters for the dissociation of nickel (II)-isoquinoline complexes in nonaqueous solvents have been measured kinetically by stopped-flow spectrophotometry (Chattopadhyay and Kratochvil, 1976, 1979). The measurements have been interpreted in light of a dissociative interchange mechanism. The dissociation rate constants obtained do not seem to correlate with Gutmann's donicity scale for solvents, but the values of  $\Delta H^\ddagger$  for the dissociation do show a linear correlation with donor number. This correlation is rationalized from a mechanistic point of view by including the effects of solvent molecules coordinated to the metal ion on the stability of the activated complex.

An investigation of the effect of added cosolvent on the kinetics of alkaline hydrolysis of  $[\text{Fe}(\text{phen})_3]^{2+}$  was carried out by Blandamer *et al.* (1978). The investigators also attempted to estimate the effect of a cosolvent on the initial state of the complex and on the transition state. It was found that in methanol-water mixtures the transition state is stabilized to a lesser degree than the initial state as the mole fraction of methanol increases; in acetone-water mixtures the reverse trend was observed. For both systems, the observed rate constant increased as the mole fraction of cosolvent increased.

Ligand Substitution in Nonaqueous Solutions. The ligand substitution kinetics of nickel (II) and other labile metal ions are much more sensitive to the nature of the ligand in nonaqueous solvents than in water (Coetzee, 1978).

Therefore it is to be anticipated that a change in solvent could alter the kinetics in a complex manner. A change in solvent could result in changes in the leaving group, in the remaining inner-sphere ligands, in the composition of the outer sphere, in the structure of the bulk solvent, and even in a change in mechanism of substitution. Studies of substitution reactions involving unidentate ligands seem to favor a dissociative interchange mechanism for six-coordinate complexes of nickel (II), cobalt (II), and manganese (II). The specificity observed in non-aqueous solvents is thought to originate in ligand-solvent interactions in the outer-sphere complexation step.

Behavior of Mixed Solvents. The relative solvating powers of two solvents for a given cation depend on properties of both the cation and the solvent, but correlate better with properties such as solvent basicity than with dielectric constant or dipole moment. In mixtures of non-aqueous solvents, cobalt (II) is solvated much more strongly by dimethyl sulfoxide than by acetonitrile; however, nickel (II) is more strongly solvated by water than by dimethylformamide (Burgess, 1978).

Statement of Research Problem. While the dissociation of trigonal bipyramidal five-coordinate complexes by acid has been studied in aqueous solution, no such studies have been carried out in nonaqueous or mixed media. If the dissociation is viewed as a concerted ligand substitution pro-



cess, it is evident that very little information about the mechanism of dissociation is available; there is conflict between associative and dissociative interchange mechanisms in the few studies which have been undertaken. This dissertation presents the results of our attempts to further explain how these complexes react.

## II. MATERIALS AND METHODS

Reagents. Reagent grade hydrated metal perchlorate salts ( $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , G. Frederick Smith Chemical Co., Columbus, OH;  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , Alfa Products, Danvers, MA) were used to prepare the five-coordinate complexes as described below.

Spectrophotometric grade N,N-dimethylformamide, dimethyl sulfoxide, and acetonitrile (Aldrich Chemical Co., Inc., Milwaukee, WI) were used without further purification. Reagent grade chloroform was dried over calcium hydride and distilled (bp 60-61°C) onto molecular sieves. Petroleum ether was distilled from calcium hydride and collected over the boiling range 70-90°C. Nitroethane was washed with two 50- ml portions of aqueous 5% sodium bicarbonate, decanted onto dried calcium sulfate, and fractionally distilled (bp 113°C). Reagent grade dimethyl sulfoxide was purified by adding barium oxide; after 24 h it was vacuum distilled (bp 50°C, 2-3 mm). Reagent grade dimethylformamide was stirred over potassium hydroxide and distilled from barium oxide (bp 149-156°C).

Analytical reagent grade monochloroacetic acid (Mallinckrodt Chemical Works, St. Louis, MO) and reagent grade perchloric acid (70-72%, J.T. Baker, Phillipsburg, NJ) were used without further purification.

Preparation of  $\text{Me}_6\text{tren}$ . A solution of 100 ml of 0.75 M

hydrochloric acid (0.75 mol) was added to 0.25 mol tren (36.5 g) (Ames Laboratories, Milford, CT) in an ice bath. To the resulting dark red solution of tren·3HCl were added 30 ml of water, 200 ml of 88% formic acid, and 155 ml 37% formaldehyde. The mixture was refluxed at 99.7°C until the evolution of carbon dioxide appeared to have ceased. The volatile fractions were removed by vacuum distillation. The residue was treated with 400 ml of 10% sodium hydroxide; excess sodium hydroxide was added until an oily layer formed. This oily layer was extracted with ether and dried over potassium hydroxide. After removal of the ether by rotary evaporation, the compound tris-(2-dimethylaminoethyl)-amine distilled as a clear oil (bp 78-83°C, 0.65 mm). Analysis by NMR yielded a singlet at 2.2 ppm and a quartet at 2.5 ppm. Integration ratio calculated 18:12 (75:50), found 73:47.

Preparation of Et<sub>6</sub>tren. Tris-(diethylaminoethyl)-amine was prepared by the method of Mizzoni, Hennessey and Scholz (1954). 2-Chloroethyldiethylamine hydrochloride (0.2 mol) was dissolved in water and the solution was saturated with sodium hydroxide to liberate the free base as an oily layer. The oil was added to 0.1 mol N,N-diethylethylenediamine with stirring and moderate heat until reaction occurred. The oil was separated by adding 100 ml of water saturated with sodium hydroxide to the product. The oil was taken up in dichloroethane and the solution was dried over potassium hydroxide. Excess solvent was removed by rotary evaporation. The product distilled as a pale yellow oil (bp 78°C, 0.02 mm). The NMR

spectrum shows a triplet at 1 ppm and a triplet superimposed on a quartet at 2.5 ppm. The experimental integration ratio is 35:50 (28:40); calculated ratio 18:24 (30:40).

Preparation of  $[M(\text{Me}_6\text{tren})X]X$  Complexes. Complexes were prepared by the method of Ciampolini and Nardi (1966). To a hot solution (50-55°C) of the appropriate metal salt in 20 ml of absolute ethanol (Rossville Gold Shield, IMC Chemical Group, Terre Haute, IN) was added dropwise with stirring a solution of 5 mmol of ligand in 10 ml of ethanol ( $\text{Me}_6\text{tren}$ ) or methanol ( $\text{Et}_6\text{tren}$ ). The perchlorate complexes separated from the mixture as crystalline solids.  $[M(\text{Me}_6\text{tren})(\text{ClO}_4)](\text{ClO}_4)$  complexes were recrystallized by dissolving then in chloroform or nitroethane and adding petroleum ether to the filtered solution.  $[M(\text{Et}_6\text{tren})(\text{ClO}_4)](\text{ClO}_4)$  complexes were recrystallized from ethanol.

Anal. Calcd for  $\text{C}_{12}\text{H}_{30}\text{N}_4\text{O}_8\text{CoCl}_2$ : C, 29.52; H, 6.19; N, 11.48. Found: C, 28.77; H, 6.45; N, 11.20.

Experimental Control. All solvent mixtures were prepared on a weight percent basis. In order to ensure reproducibility of the solvent composition in related experiments, the following technique was used.

Specific volumes of water were measured in appropriate volumetric pipettes and weighed into volumetric flasks. The flasks were then filled to the calibration mark with the nonaqueous component of the mixture and again weighed. This technique provided both volume and weight percents.

Spectrophotometric Characterization of Reactants and Products. The characterizations of the complex solutions were made spectrophotometrically with a Cary-14 spectrophotometer. The spectra were obtained at room temperature with specific compositions of solvent mixtures. Complex solutions were mixed on a 1:1 basis with solutions of the dissociating agent to verify that complete dissociation takes place under the experimental conditions.

Kinetic Measurements. The dissociation reactions were followed by means of a Durrum-Gibson stopped-flow single-beam spectrophotometer with a Kel-F flow path and a 2-cm path length cuvette. All reactions were studied at constant temperature within the range of 5.0°C to 35.5°C, with a precision of  $\pm 0.1^\circ\text{C}$ . The reactant solutions in the drive syringes, the Kel-F flow path, and the reaction cuvette were contained in a water reservoir connected in continuous flow with a NesLab RTE-8 thermostat bath.

The output information from the stopped-flow instrument was recorded on a Tektronix RM564 oscilloscope as a trace of voltage versus time. Deionized water, specific solvents, or water-solvent mixtures were used as references in such a way as to relate linearly the voltage scale of the oscilloscope to percent transmittance in the 0% to 100% range.

The analog signal recorded on the oscilloscope was photographed on Polaroid film. Digitalization of the data was performed manually with an arbitrary decimal scale for the voltage. The horizontal scaling grid of the oscilloscope

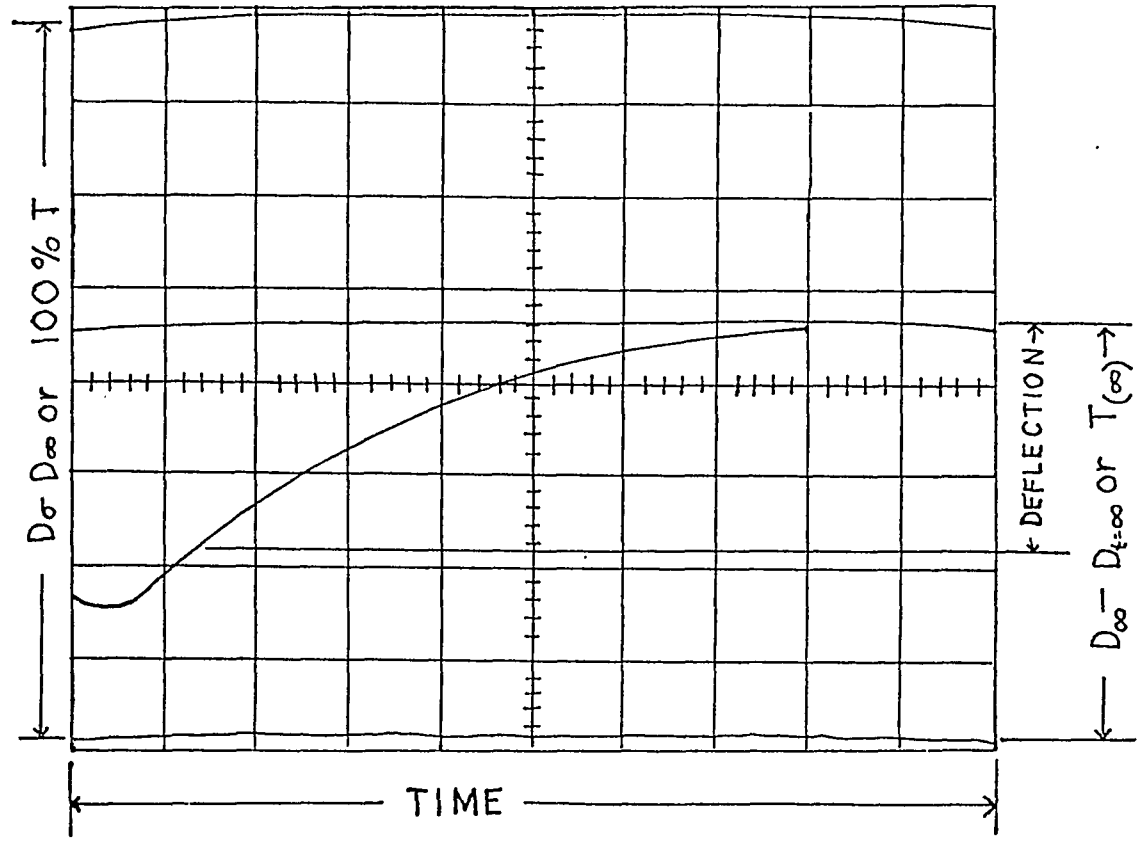
output was used as the time scale. Data manipulation to yield plots of log A versus time was carried out by use of the TRDATA program as adapted for the DEC-10 computer. First-order rate constants were determined from these plots (see Figures 2-1 and 2-2).

Setting of Experimental Conditions. The concentration of metal complex throughout the experiments was chosen to be  $2.0 \times 10^{-3}M$  ( $1.0 \times 10^{-3}M$  in the reaction cuvette). This concentration allows the system to obey Beer's Law while being sufficient to produce a readily observable signal change upon dissociation. The concentration chosen causes a change of approximately 0.15 absorbance units, or 0.1 volt on the oscilloscope. Chloroacetic acid solutions were  $2.0M$  ( $1.0M$  in the reaction cuvette); however, perchloric acid solutions were  $0.5M$  ( $0.25M$  in the reaction cuvette) to minimize the amount of water introduced into the nonaqueous systems.

Not all systems could be studied over the entire temperature range chosen. The dimethyl sulfoxide studies, for example, were limited to temperatures above  $18^{\circ}C$  because of the freezing point of the solvent. Other constraints upon the range of possible experimental conditions include the rate of the reaction at higher temperatures, the increase in vapor pressure of the solvent with increased temperature, and the change in solvent composition.

The nonaqueous dissociation appears to be a multiple step reaction. By adjusting the oscilloscope time base it was possible to separate two discrete steps, hereinafter

Figure 2-1. Representation of the oscilloscope trace obtained from a kinetic run in which absorbance decreases as a function of time.



TIME	DEFLECTION	ABSORBANCE	LOG10 (D(T) - D(INF))	D(T) - D(INF)
0.0	76.50	0.4640E-01	-0.18590E+01	0.1383E-01
2.00	64.50	0.4420E-01	-0.19342E+01	0.1163E-01
4.00	57.00	0.4283E-01	-0.19886E+01	0.1027E-01
6.00	50.50	0.4165E-01	-0.20418E+01	0.9083E-02
8.00	44.00	0.4047E-01	-0.21022E+01	0.7903E-02
10.00	37.00	0.3920E-01	-0.21781E+01	0.6636E-02
12.00	32.50	0.3839E-01	-0.22348E+01	0.5823E-02
14.00	28.00	0.3758E-01	-0.23000E+01	0.5012E-02
16.00	24.00	0.3686E-01	-0.23673E+01	0.4293E-02
18.00	21.00	0.3632E-01	-0.24255E+01	0.3754E-02
20.00	18.50	0.3587E-01	-0.24808E+01	0.3305E-02
22.00	16.00	0.3542E-01	-0.25441E+01	0.2857E-02
24.00	13.50	0.3498E-01	-0.26181E+01	0.2410E-02

Figure 2-1.



Figure 2-2. Representation of the straight line obtained by using the TR-DATA program to plot change in absorbance as a function of time. The rate constant is determined from the slope of the line.

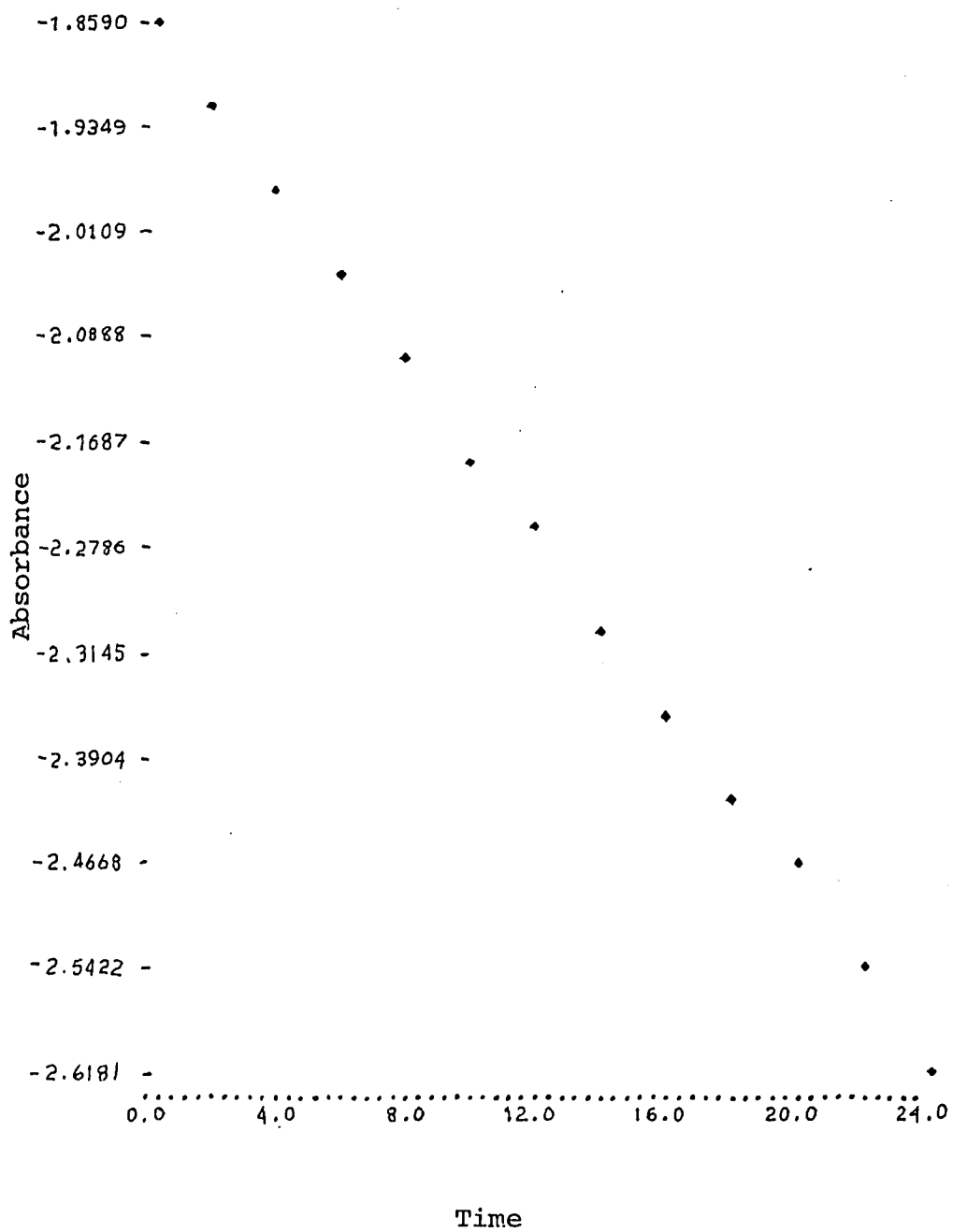


Figure 2-2.

referred to as the fast step and the slow step. Because the fast step was more rapid by several orders of magnitude than the slow step, appropriate adjustment of the time base made it possible to study these steps as independent first-order processes.

### III. RESULTS AND DISCUSSION

The results show that in the solvents used, the dissociation of the cobalt (II) complex proceeds via multiple steps. The initial rapid dissociation step involves the greatest change in absorbance and is therefore thought to correspond to the loss of five-coordination, inasmuch as six-coordinate cobalt species have relatively much smaller molar absorptivities. At least one slower step has been characterized as first order, but the absorbance change for any subsequent step is very small and cannot be measured with sufficient accuracy to yield useful kinetic information under the reaction conditions employed. A method suitable for possible further investigation of the slower steps is discussed (vide infra).

Acid Dependence. The dissociation is a first-order process, depending entirely on the concentration of complex. The first-order rate constant exhibits no dependence on acid concentration in the range studied (0.25-1.0M). The dissociation requires acid to be present, because the complex itself is indefinitely stable when solvent alone is present. The acid may be involved in a step which is not rate-determining, because it does not itself appear in the rate equation.

However, it is also possible that the rate constant

$k_{\text{obs}}$  contains within it a constant which is a measure of acid concentration. This value, if such exists, is exceeded in the range studied and therefore the reaction rate appears to be independent of acid concentration. If  $k_{\text{obs}}$  does actually contain within it a constant which depends on acid concentration if the acid concentration were sufficiently low. This may explain the fact that the reaction does not occur except in the presence of acid. This type of behavior has been observed when solvent coordinated to  $\text{Me}_6\text{tren}$  complexes is replaced by a ligand molecule (Lincoln, 1979).

Results of the reaction order studies are shown in Table I.

Dissociation of  $\text{Co}(\text{Me}_6\text{tren})^{2+}$ . Results of the dissociation of the cobalt (II) complex in various solvents are presented in Table II. In water at 298 K, dissociation by 1.0 M chloroacetic acid is comparatively slow ( $3.56 \text{ s}^{-1}$ ), but is still faster than that reported for dissociation by 1.0 M perchloric acid ( $1.36 \text{ s}^{-1}$ ). The rate constant for the dissociation in acetonitrile is very similar ( $4.05 \text{ s}^{-1}$ ). This is consistent with the low Gutman donor numbers for each solvent. These values have been chosen as a means of correlating solvent properties with the rate constants observed, as will be discussed below and in the section on mechanistic considerations.

In dimethyl sulfoxide, the rate constant is double ( $9.38 \text{ s}^{-1}$ ) that for acetonitrile; likewise the rate constant for the dissociation in dimethylformamide is double ( $18.4 \text{ s}^{-1}$ )

Table I. Studies of the dependence of reaction rate on the concentration of metal complex and of acid in dimethylformamide at 298 K.

$k$ ( $s^{-1}$ )	$[Co(Me_6tren)]^{2+}$ (M)	$[HA]$ (M) ***
*18.4	$1.0 \times 10^{-3}$	1.0
*17.3	$5.0 \times 10^{-3}$	1.0
*20.4	$5.0 \times 10^{-4}$	1.0
**10.5	$1.0 \times 10^{-3}$	1.0
** 8.08	$1.0 \times 10^{-3}$	0.5
** 5.86	$1.0 \times 10^{-3}$	0.25

\* in 1.0M  $NaClO_4$ . \*\* in 0.8M  $NaClO_4$ .

\*\*\* HA = chloroacetic acid.

Table II. Rate constants for the dissociation of  $[Co(Me_6tren)]^{2+}$  in various solvents at 298 K.

Solvent	$k$ ( $s^{-1}$ )
Water	3.56
Acetonitrile	4.05
Dimethyl sulfoxide	9.29
Dimethylformamide	18.4

Table III. Solvent properties.

Solvent	$\epsilon^*$	$\alpha^{**}$	Donor Number*	$E_T$ (kcal mol <sup>-1</sup> )*
Water	78.5	1.47	18	63.1
Acetonitrile	37.5	4.5	14.1	46.0
Dimethyl sulfoxide	48.9	8.0	29.8	45.0
Dimethylformamide	36.7	7.9	26.6	43.8

\* Burgess, p.32.

\*\* Coetzee, p.81.

Table IV. Arrhenius parameters for the dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  by 1.0 M chloroacetic acid in various solvents.

Solvent	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	ln A
Water	52.4	49.9	-73.1	22.4
Dimethyl sulfoxide	53.1	50.6	-56.6	23.7
Dimethylformamide	55.9	53.4	-48.0	25.4

that for dimethyl sulfoxide.

Table III presents some solvent properties which may be significant in explaining these differences.

Gutmann Donor Numbers. The Gutmann donor number is a measurement of the electron donating capacity of the solvent, as determined by its enthalpy of reaction with antimony pentachloride in 1,2-dichloroethane as solvent (Gutmann and Schmid, 1974). Although water has the highest dielectric constant of the solvents studied, its polarizability is the lowest; the inductive effect of the methyl groups of the other solvents contributes to the increased nucleophilicity of these solvents. It is to be expected that a strongly basic solvent would interact more readily with a Lewis acid such as the cationic cobalt center.

The fact that dimethylformamide, with lower polarizability and lower donor number, shows a rate constant double that of dimethyl sulfoxide may be attributable to the steric hindrance to insertion of the planar dimethyl sulfoxide molecule into the inner sphere. The more linear dimethylformamide molecule may fit more easily between the ligand groups (see Figure 3-1).

Activation Parameters. Arrhenius parameters have been calculated for the dissociation in each solvent studied, and are presented in Table IV. The activation energies are similar enough ( $52.4 \text{ kJ mol}^{-1}$  in water,  $53.1 \text{ kJ mol}^{-1}$  in dimethyl sulfoxide, and  $55.9 \text{ kJ mol}^{-1}$  in dimethylformamide) to suggest the conclusion that the same rate-determining step prevails in all solvents studied. The high values calculated for



Figure 3-1. Representations of the solvent molecules water, acetonitrile, dimethyl sulfoxide and dimethylformamide.



the pre - exponential factor,  $\ln A$  (22.4 in water, 23.7 in dimethyl sulfoxide and 25.4 in dimethylformamide) are indicative of an increase in order in the transition state. Such an increase is borne out by the large negative values of the transition state entropy (-78.1 e.u. in water, -56.6 e.u. in dimethyl sulfoxide and -48.0 e.u. in dimethylformamide). Thus the activation parameters seem to indicate that a similar reaction pathway is followed in each solvent. The difference in the rate constants must be attributed to the solvents themselves.

Dissociation Mechanisms. Two mechanisms may be put forward to explain the dissociation of five-coordinate complexes in the various solvents. The dissociative mechanism (Figure 3-2) is based on the rate-determining spontaneous dissociation of one arm of the ligand from the metal ion. Because of the high concentration of acid present in an aqueous medium, the amine group on this arm is quickly protonated, thus preventing its reassociation to the metal ion. At this point, the complex has become more tetrahedral in geometry, and has become tripositive. A solvent molecule is then able to enter the inner sphere and coordinate to the metal ion in the position vacated by the ligand arm. The complex is again five-coordinate; however, the increased charge renders it more susceptible to nucleophilic attack by the solvent and the ligand is rapidly replaced by four more solvent molecules. The product is a hexa-solvated metal (II) species. This is a postulated mech-

Figure 3-2. Scheme of the proposed dissociative mechanism for the dissociation of five-coordinate complexes.

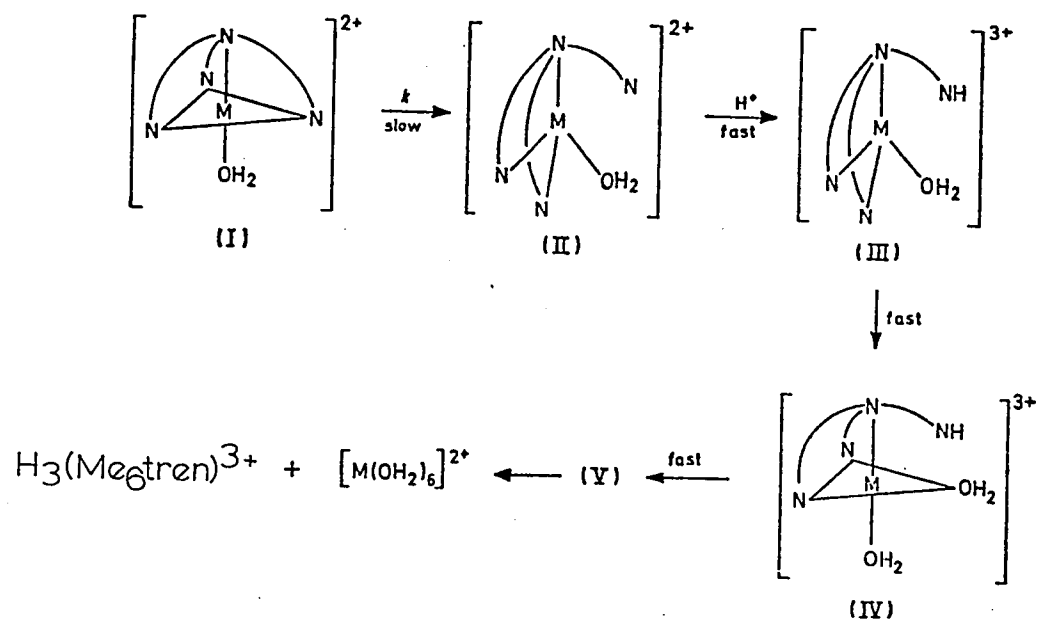


Figure 3-2.

anism for the dissociation of five-coordinate complexes by acid in aqueous solution (Lincoln and Hubbard, 1974).

Another plausible mechanism for dissociation is shown in Figure 3-3. In this associative mechanism, the rate-determining step is the initial insertion of a solvent molecule, in the presence of acid, into the inner sphere. Six-coordination is therefore achieved early in the reaction. While the rate of this insertion may depend on the solvent involved, it does not occur unless acid is present. The acid must act to loosen the metal-to-nitrogen bonds, either because of attraction of the electrons on the donor nitrogens to the hydrogen ions produced by a strong acid or because of similar attraction to the positively polarized hydrogens of a partially dissociated weak acid. Such loosening of these bonds facilitates subsequent attack by the solvent molecules and culminates in the complete dissociation of the ligand from the metal ion. The slower reaction step which has been observed may correspond to the rearrangement of the components of an already six-coordinate complex.

Alternatively, the steric requirements of the hexamethylated ligand may be such that forced six-coordination, by pushing the equatorial nitrogens closer together, may strain the bonds within the two joined methylene groups. Rather than the energetically unfavorable rupture of carbon-carbon or carbon-nitrogen bonds, it is the dative covalent bond between the metal ion and the ligand nitrogen which is

Figure 3-3. Scheme of a possible associative mechanism for the dissociation of five-coordinate complexes.

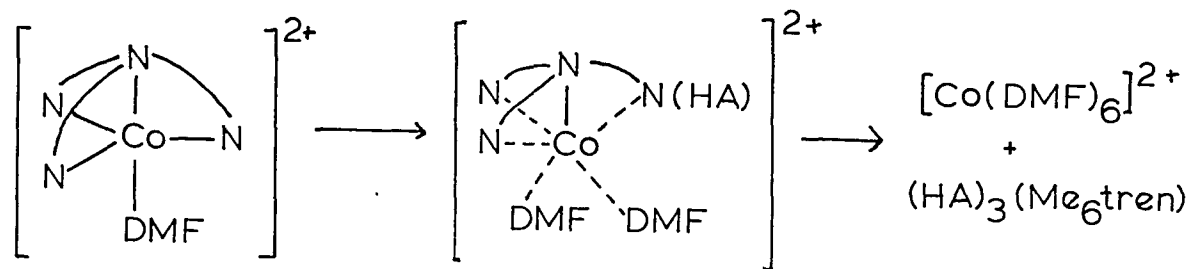


Figure 3-3.



broken. Because six-coordination is the "normal" state for cobalt (II), the presence of nucleophilic solvent molecules allows the metal ion to assume its preferred geometry.

The aqueous dissociation of five-coordinate complexes of nickel (II), cobalt (II) and copper (II) via the dissociative mechanism described above has been shown to proceed via a kinetic process with a single rate-determining step. (The possibility exists, of course, that slower steps with extremely small absorbance changes are occurring but are simply not detectable under the reaction conditions employed.) The dissociation of six-coordinate transition metal complexes such as tris-ethylenediamine nickel (II) in aqueous acid solution proceeds via a series of stepwise dechelation reactions (Ahmed and Wilkins, 1960; Kemp et al., 1979). The rate-determining step at each stage of the dissociation is the rupture of the nickel-nitrogen bond. Each stage has been found to be slower than the preceding one, i.e., the first ligand is more quickly dissociated than the second, and the second more quickly than the third. In aqueous perchloric acid at 298.0 K rate constants of  $87 \text{ s}^{-1}$ ,  $5.2 \text{ s}^{-1}$ , and  $0.15 \text{ s}^{-1}$  have been observed for the first, second, and third dechelations, respectively. Such findings would be consistent with the results reported in this work for reactions in non-aqueous systems. If six-coordination is rapidly achieved as a result of solvent insertion, the subsequent slower steps could then represent the unwrapping of the ligand from the metal. In aqueous solution, reaction within the framework

of the dissociative mechanism occurs with the attainment of six-coordination at a later stage of the dissociation; therefore the gradual unwrapping of the ligand from the metal ion is replaced by a rapid, concerted removal of the ligand.

Mechanistic Considerations. These mechanisms can be described as nucleophilic substitution reactions of the type  $S_N1$  (lim) for the dissociative mechanism, and  $S_N2$  (lim) for the associative mechanism (Basolo and Pearson, 1958). The  $S_N1$  (lim) mechanism is characterized by a large degree of bond breaking in the rate-determining step with no concurrent bond making, and by definite evidence for an intermediate of reduced coordination number. The dissociative mechanism for the dissociation of the metal complex likewise involves bond breaking in the rate-determining step and a change in coordination number from five to four.

Conversely, the  $S_N2$  (lim) mechanism is characterized by a large degree of bond making in the rate-determining step with no concurrent bond breaking, and definite evidence for an intermediate of increased coordination number. The proposed associative mechanism for the dissociation of the metal complex involves nucleophilic attack by a solvent molecule in the presence of acid, and concomitant increase in coordination number from five to six. Bond breaking occurs subsequent to the rate-determining step.

The  $S_N1$  (lim) mechanism is a dissociative rather than a displacement mechanism; the energy interaction between

leaving group and entering group is small. However, in the  $S_N2$  (lim) mechanism the energy interaction is large and is dependent on solvent properties.

Acceleration in reaction rate upon increased substitution is strongly suggestive of a dissociative mechanism. Preliminary studies in aqueous perchloric acid solution have indicated that the rate increases as the ligand substituent increases in bulk ( $k_H < k_{CH_3} < k_{CH_2CH_3}$ ). Inductive effects contribute to the base-strengthening character of the alkyl groups with respect to hydrogen.

Application of Crystal Field Stabilization Energies in Kinetics. Crystal field stabilization energies are used most frequently in equilibrium situations, i.e., in predicting stabilities and spectra of complexes at equilibrium. The importance of crystal field stabilization energies in determining the rates of reaction of coordination complexes has been described qualitatively (Orgel, 1952) as well as quantitatively (Basolo and Pearson, 1958). For substitution reactions of octahedral complexes, the procedure described involves calculating the crystal field stabilization energy for the appropriate number of d electrons for a regular octahedral complex, a regular square pyramid, and a pentagonal bipyramid in both a strong field and a weak field. These latter geometries are used to approximate the transition states (activated complexes) for  $S_N1$  and  $S_N2$  mechanisms, respectively. The differences between the original and final crystal field stabilization energies (because both reactant

and product are octahedral complexes) is considered as a contribution to the total activation energy for each reaction. A large contribution implies a slow reaction by that particular pathway; a negative contribution is essentially a zero value.

It is relatively rare to use crystal field stabilization energy for calculations involving differences in energy between the ground (initial) state and the transition state itself because of the assumptions which must be made about the structure of the activated complex.

Crystal field contributions to the activation energy for a transition state between five- and four-coordination, and between five- and six-coordination have been calculated, and are presented in Table V. The crystal field activation energy associated with the dissociative mechanism is positive for all metals studied; the transition state must be more reactant-like than product-like, and the reaction is relatively slow. For a change in coordination number from five to six, as is postulated for the transition state for the associative mechanism, the crystal field activation energy is negative, or therefore essentially zero, for cobalt (II) and nickel (II); clearly the six-coordinate state is favored and the metal ion will try to attain it if possible. The transition state in this case is product-like.

Crystal field theory makes predictions not about the absolute rates of these reactions, but about the relative rates for systems with different numbers of d electrons, with different orbital hybridizations, or with different

Table V. Crystal field activation energies.

	<u>5→4</u>	<u>5→6</u>
Co(II)	0.10 Dq	-2.56 Dq
Ni(II)	2.70	-5.74
Cu(II)	5.30	1.08

Table VI. Percent dissociation of 2.0 M chloroacetic acid in dimethylformamide/water mixtures at 298 K based on conductivity studies.

<u>% water</u>	<u>α x 100</u>
0	0.04 o/o
2.5	0.13
5	0.14
10	0.19
20	0.21
25	0.29
50	0.52
75	1.01
100	1.73

geometries. The absolute rate is determined largely by the charge on the metal atom, the nature of the ligands, and other constraints of the system.

Role of Solvent. While first-row transition metals prefer to bond to nitrogen rather than oxygen, the properties of the solvent play an important role in determining whether the reaction pathway to be followed will be  $S_N1$  (lim) or  $S_N2$  (lim). Increasing the negative charge on the entering group will have no effect on the rate of reaction if the mechanism is  $S_N1$ ; the rate will increase with increasing negative charge if the mechanism is  $S_N2$ . Increasing the size of the entering group again will not affect the rate for an  $S_N1$  (lim) mechanism; it will decrease the rate for an  $S_N2$  (lim) mechanism. Increasing the size of the leaving group, i.e., by increasing the size of the substituents, will increase the rate of an  $S_N1$  (lim) reaction, but will decrease the rate of an  $S_N2$  (lim) reaction.

The solvents studied are very similar in size and shape, as seen in Figure 3-1. Although water and acetonitrile are small molecules and therefore should increase the rate when they constitute the entering group, the electron density available to the metal ion from the entering nitrogen or oxygen is diminished relative to that of the larger dimethylformamide and dimethyl sulfoxide molecules. The increase in availability of electrons to the metal ion may be explained in terms of the inductive effect of the methyl groups present in these solvent molecules. This increased availability is reflected

in the Gutmann donor numbers for these molecules. In addition, the unsaturation of these solvent molecules increases their effectiveness as displacing reagents because of the chance for increased bonding in the transition state. Therefore the rate constants within the framework of an associative mechanism are expected to be higher in dimethylformamide and dimethyl sulfoxide.

Mixed Solvent Studies. Two extremes have been described in the elucidation of the mechanism of dissociation of the five-coordinate complex by acid. In order to determine the extent to which each mechanism contributes to the actual dissociation mechanism, studies were undertaken in varying mixtures of dimethylformamide/water and dimethyl sulfoxide/water. Results of several of these studies are presented in Figure 3-4(a-d). In all cases the addition of a small amount of water (<5%v/v) resulted in an increase in the rate constant for the reaction. Addition of larger amounts of water resulted in decreasing values of  $k_{obs}$ ; above 50% (v/v) the observed rate constant approximates the value observed in aqueous systems ( $k=3.56s^{-1}$  for dissociation by 1.0M chloroacetic acid,  $1.36s^{-1}$  for dissociation by 1.0M perchloric acid).

In mixed solvents, it is also necessary to consider the possibility of interactions between the different solvent molecules. Water, dimethylformamide, and dimethyl sulfoxide all are strong hydrogen-bonding solvents; solvent-solvent interactions cannot be

Figure 3-4. Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K.

(a) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylformamide by 1.0M chloroacetic acid in the presence of 1.0M sodium perchlorate.



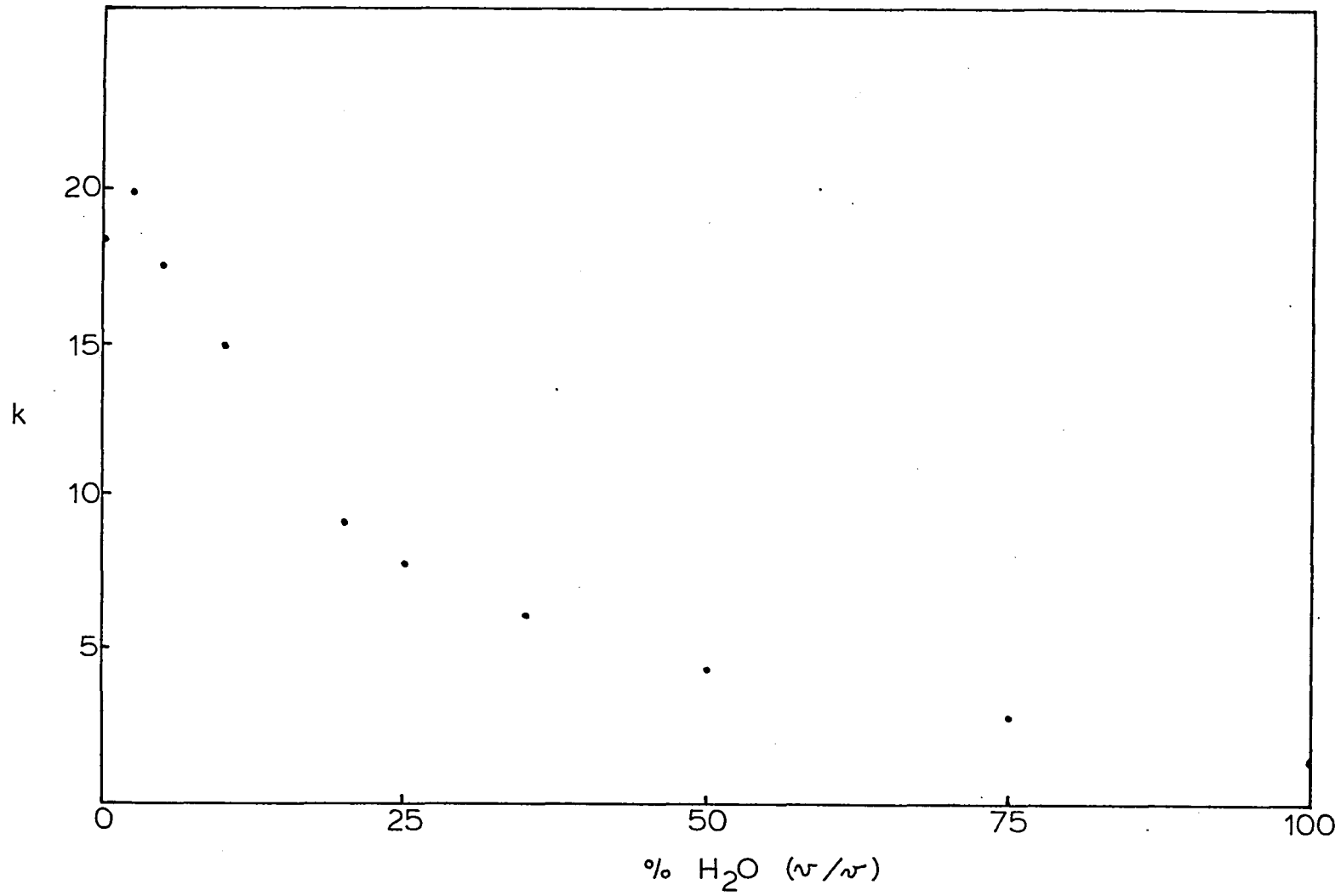


Figure 3-4 (a).

Figure 3-4. Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K.

(b) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylformamide by 1.0M chloroacetic acid in the absence of inert electrolyte.

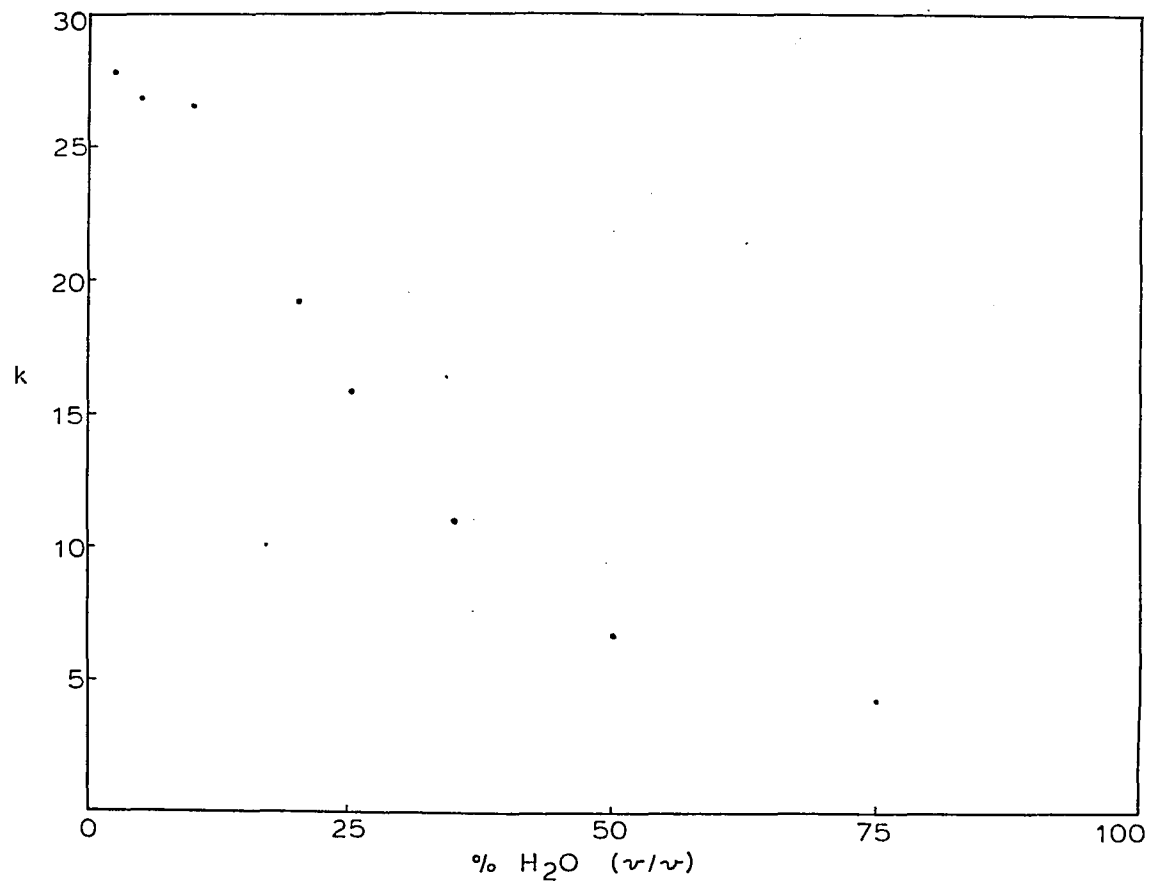


Figure 3-4 (b).

Figure 3-4. Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K.

(c) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylformamide by 0.25M perchloric acid in the absence of inert electrolyte.

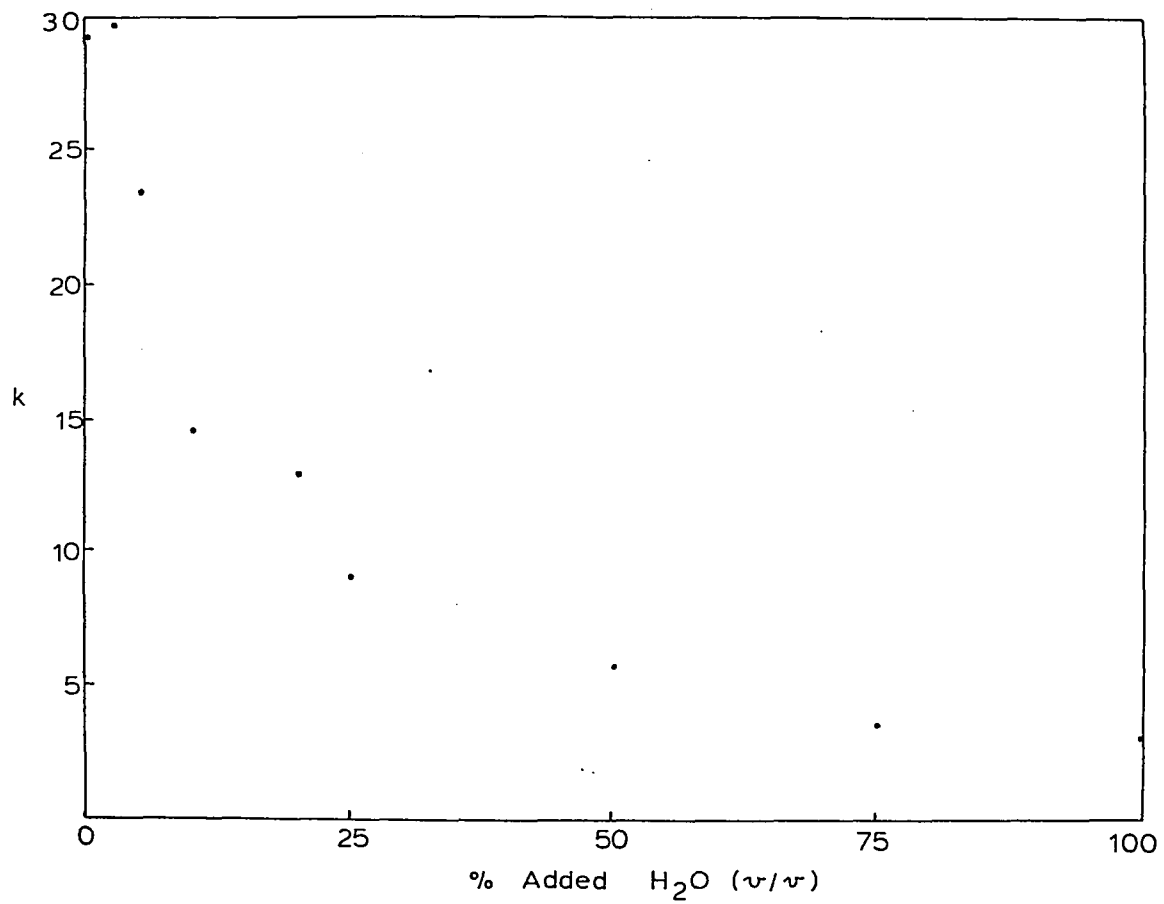


Figure 3-4 (c).

Figure 3-4. Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K.

(d) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethyl sulfoxide by 1.0M chloroacetic acid in the absence of inert electrolyte.

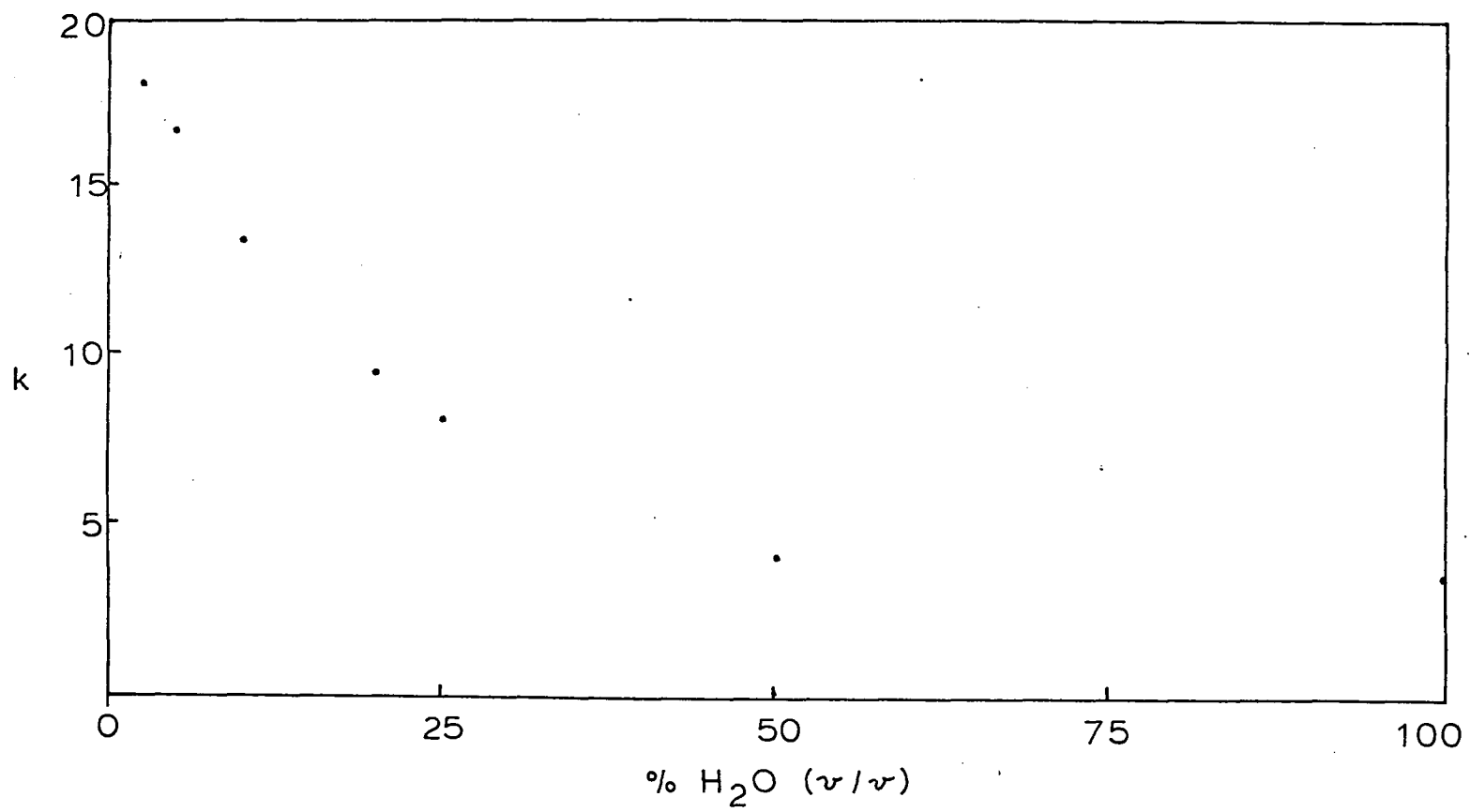


Figure 3-4 (d).

ignored in dimethylformamide/water and dimethyl sulfoxide/water mixtures.

The increase in rate constant in mixtures containing less than 10% water by volume may be attributable to hydrogen bonding between water molecules and solvent. The net effect would therefore be an increase in the availability of electrons from nucleophilic water (solvent) to the metal ion. If nucleophilic attack in the presence of acid is the rate-determining step, then increasing the percent water in the mixture should continue to increase the rate of dissociation. The fact that the rate begins to decrease in mixtures of greater than 10% water by volume seems to indicate that an acid-assisted association is not favored when sufficient water is present.

(Although both the dimethylformamide and the dimethyl sulfoxide used in these experiments were of spectroscopic quality, it is unlikely that either was truly anhydrous. Because the solutions were prepared in an open laboratory rather than under dry box conditions, it was difficult to keep out trace water. This may be very important, because the fifth coordination position of the complex in solution may have been occupied by water rather than a solvent molecule. Because the complex concentration in these studies was  $1.0 \times 10^{-3} \text{ M}$ , a concentration of water on the same order would be sufficient to aquate every complex molecule, and therefore the effects attributed to the presence of water may already be operative in the "anhydrous" solutions.)

A second explanation of the kinetic behavior of the



system in mixed solvents involves the effect of water on the acid molecules in the solution. In nonaqueous solvents, monochloroacetic acid does not measurably dissociate. Protons are not available, but the entire acid molecule may hydrogen bond to the amine, thus weakening the metal-nitrogen bond because of electrostatic interactions and because of steric effects. As water is introduced into the system in increasing amounts, the degree of dissociation of the acid increases, as shown in Table VI. The availability of protons (as  $\text{H}_3\text{O}^+$ ) and the difference in accessibility of the amine nitrogen to the smaller molecule, provide several possible implications for the reaction. First, hydrogen bonding between water and solvent molecules may decrease, because the water molecules are more likely to be protonated. For example, in a 10% water mixture, the molar concentration of water in the system is 5.56 M. The percent of the chloroacetic acid dissociated in this mixture is 0.19%. Therefore the 1.0 M acid solution produces a solution of hydrogen ion which is 0.0019 M. Obviously this effect will be small.

Second, charge interactions may be occurring between the hydronium ions and the solvent nucleophilic sites, thereby decreasing their availability to the metal ions. In a 10% (v/v) water/dimethylformamide mixture, the water concentration is 5.56 M and the dimethylformamide concentration is 11.68 M. If the hydronium ion concentration is 0.19 M the concentration of dimethylformamide available to the metal ion is still 11.68 M. Again, the effect is negligibly small.

Third, interactions between hydronium ion and ligand nitrogen increase as the percent water in the solvent mixture increases. The smaller hydronium ions can more readily attack the nitrogen atoms than can the bulky chloroacetic acid molecules. Instead of forming a loose adduct, the hydronium ion can physically approach close enough to bond to the electron-rich nitrogen. The effective charge of the metal is less than the charge of the hydronium ion, and the electron pair of nitrogen can therefore be attracted away from the metal ion. Reformation of the metal-nitrogen bond is prevented because of electrostatic interactions, and dissociation via a dissociative pathway is initiated. In a solution which is  $1.0 \times 10^{-3}$  M in complex molecules, a  $1.9 \text{ mM}$  hydronium ion concentration is sufficient to provide bonding to every ligand nitrogen available. This excess of hydronium ions around the outer solvation sphere may actually inhibit associative solvation of the metal due to repulsion between the cationic center and the positively charged ions.

Effect of Ionic Strength. Studies of the dissociation of cobalt (II) complexes in aqueous solution were previously undertaken in the presence of  $2.0 \text{ M}$  sodium perchlorate. This was done to maintain a constant ionic strength and to prevent any mixing heterogeneities in the stopped-flow spectrophotometer which might arise from mixing a concentrated ( $1.0 \text{ M}$ ) acid solution with a dilute ( $1.0 \times 10^{-3} \text{ M}$ ) complex solution. The constant ionic strength swamps out small changes over the course of the reaction. The heterogeneities can cause

artifacts in short time periods (50 milliseconds) and therefore interfere with the measurement of faster kinetic processes. Initial studies in acetonitrile were conducted at an ionic strength of 1.0 M and later of 0.8 M. No significant differences in the rate constants were observed at these lower concentrations of sodium perchlorate.

When chloroacetic acid was used as the dissociating agent, sodium chloroacetate was chosen to maintain the ionic strength of the system. However, sodium chloroacetate proved insoluble in the nonaqueous reagents. Therefore subsequent studies were conducted without the addition of an electrolyte to the reagent solutions. No significant experimental problems were encountered as a consequence of the absence of an inert electrolyte although there are kinetic consequences.

Some interesting differences in the rate constant were immediately apparent, as shown in Table VII and Table VIII. In both dimethylformamide/water mixtures and in dimethyl sulfoxide, addition of 1.0 M sodium perchlorate to the reagent solutions caused a decrease in the observed rate constant of as much as fifty percent. These differences can be explained in part by the Debye-Hückel theory, which can be used to predict the influence of ionic strength on the rate of reaction. For very dilute solutions, if one of the reactants is a neutral molecule (such as a solvent molecule), ionic strength is predicted to have no effect on the reaction. However, if the rate of reaction depends on the degree of dissociation of a weak acid (such as chloroacetic acid) then

Table VII. Effect of added inert electrolyte on rate constant for the dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  by 1.0M chloroacetic acid at 298 K.

Solvent	k (with $\text{NaClO}_4$ )	k (without $\text{NaClO}_4$ )
Water		3.56 $\text{s}^{-1}$
Acetonitrile	4.02 $\text{s}^{-1}$	
Dimethyl sulfoxide	4.49	9.38
Dimethylformamide	18.4	16.8

Table VIII. Rate constants for the dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  by 1.0M chloroacetic acid in dimethylformamide/water mixtures at 298 K in the presence and absence of inert electrolyte.

% water	k (with $\text{NaClO}_4$ )	k (without $\text{NaClO}_4$ )
0	18.4 $\text{s}^{-1}$	16.8 $\text{s}^{-1}$
2.5	20.3	27.8
5	17.9	26.7
10	14.9	26.5
20	9.12	19.2
25	7.80	15.8
35	6.14	11.0
50	4.37	6.63
75	2.84	4.23
100		3.56

the rate of the reaction will depend on the salt concentration. This theory offers an explanation of ionic strength dependence, which is valid up to an electrolyte concentration of 0.01 M; above that the Debye-Hückel theory is no longer applicable, although there is still an (unexplained) effect of ionic strength on rate.

If the ionic strength is kept constant at some large value which does not change appreciably over the course of the reaction, then "swamping" of the reaction is occurring. Rate constants obtained in this manner are generally quite different from those in very dilute (ideal) solutions. Providing comparably high ionic strengths are used, it is still possible to compare kinetic parameters from different studies.

The fact that the observed rate constants decrease dramatically in the presence of 1.0 M sodium perchlorate in both dimethyl sulfoxide and dimethylformamide must mean that a high ionic strength medium does not facilitate the formation of the activated complex, or that it stabilizes the ground state further with respect to the transition state. The reduction in rate constant is due to a composite effect of the electrolyte on the ground state and/or transition state, which may arise from solvent (medium) changes brought about by the presence of the electrolyte.

Effect of Dielectric Constant. For a reaction between an ion and a neutral molecule, such as is assumed for the associative mechanism, the rate of reaction will be larger in a medium of lower dielectric constant. The dielectric constants of dimethylformamide (36.7) and dimethyl sulfoxide

(48.9) are considerably lower than the dielectric constant of water (78.5). Solvents of low dielectric constant are not able to solvate charges well and favor the formation of ion pairs. If sufficient electrolyte is added to the reaction system, the solvent molecules may no longer exist primarily as neutral species. Instead, they may form solvent-electrolyte ion pairs. Nucleophilic attack by the solvent is thus rendered unfavorable in a system of high ionic strength.

There is also the remote possibility that variation of rate constant with solvent composition may be due to dielectric constant variation. If the bulk solvent solvates either the ground state or the transition state (or possibly both) differently as the solvent composition is changed, then a different rate constant could result even if a common mechanism is operating, provided there is sufficient water present. The bulk solvent effects cause  $\Delta G^\ddagger$  to become smaller initially, then progressively slightly larger as the percent water in the solvent mixture increases. If temperature dependence measurements were available for the whole solvent range, it might be possible to separate  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  contributions to the changing  $\Delta G^\ddagger$ . Then  $\Delta S^\ddagger$  might be indicative of solvation differences.

Suggestions for Further Studies. It has been noted above that acceleration in reaction rate upon increased substitution (increased size) of the leaving group is strongly suggestive of a dissociative mechanism. Preliminary studies

of the dissociation of the ethylated ligand complex of copper (II) by 0.1 M perchloric acid in aqueous solution indicate that the rate of reaction is considerably faster than that of the corresponding methylated ligand complex ( $k_{\text{obs}} = 27.5 \text{ s}^{-1}$  at 277.9 K for the ethylated complex, versus  $27.8 \text{ s}^{-1}$  at 293 K for the methylated complex). Comparable studies involving the cobalt (II) complex should be undertaken in water, dimethylformamide, and dimethyl sulfoxide. A corresponding increase in the rate of dissociation in the latter solvents would be indicative of a dissociative mechanism.

These studies have initially proven difficult for several reasons. First, it is difficult to synthesize the ligand and the complex in large quantities. Second, the reaction is quite rapid and may approach the time limit of resolution of the stopped-flow spectrophotometer except at low temperatures which are not readily controlled by the thermostating system. Third, relatively high concentrations are required to achieve a reasonable signal amplitude, but solubility is limited at low temperatures.

Studies of complex dissociation involving methylated ligand complexes might also be performed with a rapid-scanning spectrometer such as is utilized by Moore and associates (Kemp *et al.*, 1979) to study systems of high concentration. In practice, solubility considerations may limit the concentrations which can be used. Reactions which have been investigated in this manner include the decomposition of tris-ethylenediamine nickel (II), bis-diethyl-

enetriamine nickel (II), and dihydroxytriethylenetetramine nickel (II). Detailed spectra have been obtained of certain of the intermediates, as well as the kinetics and rates of the various stages. The process of acid-catalyzed dechelation has been shown to be more complex in some cases than had previously been supposed. This approach allows one to obtain complete instantaneous displays of successive spectra of transient intermediates in a stopped-flow system and eliminates experimental scatter caused by overlapping of spectra of successive transient intermediates.

Rapid scan studies of the dissociation of the complexes could be of considerable value in detecting and attempting to characterize short-lived reaction intermediates at wavelengths other than the absorbance maximum. The results therefore would shed further light on the reaction mechanism.

Conclusions. At present, it is clear that neither a dissociative nor an associative mechanism satisfies all the requirements of the activation parameters; the actual pathway lies somewhere between the two extremes, influenced by solvent characteristics as well as by the constraints of thermodynamics, stereochemistry, and crystal field energetics.

Interpretations of kinetic data are always somewhat equivocal in light of the fact that transition state theory describes average properties. The form of the activated complex is a matter for considerable speculation, particularly in the systems studied, where the reaction involves one or more solvents and in some cases inert salts in addi-



tion to the reactants themselves. Other kinetic studies of substitution and dissociation in coordination complexes have usually involved processes in which no net change in coordination number has occurred. By contrast, in this work, in addition to all the normal difficulties encountered in analysis and interpretation, there is the change in coordination number in going from reactants to products to consider.

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APPENDICES

Supporting Data for Figure 3.4 (a)

Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K

(a) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylformamide by 1.0 M chloroacetic acid in the presence of 1.0 M sodium perchlorate: rate constants and activation parameters.

$\% \text{H}_2\text{O}$	$k(\text{s}^{-1})$	$\Delta H^\ddagger (\text{kJ mol}^{-1})$	$\Delta S^\ddagger (\text{J mol}^{-1}\text{deg}^{-1})$
0	18.4	51.6	-48.0
2.5	27.8	66.8	+6.73
5	26.7	48.8	-53.9
10	26.5	79.3	+48.2
20	19.2	69.6	+13.1
25	15.8	65.5	-2.43
35	11.0	62.6	-15.0
50	6.63	50.2	-61.0
75	4.23	48.8	-69.2
100	3.56	48.1	-73.1

Supporting Data for Figure 3.4 (c)

Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K

(b) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylformamide by 0.25 M perchloric acid in the absence of inert electrolyte: rate constants and activation parameters.

$\% \text{H}_2\text{O}$	$k(\text{s}^{-1})$	$\Delta H^\ddagger(\text{kJ mol}^{-1})$	$\Delta S^\ddagger(\text{J mol}^{-1}\text{deg}^{-1})$
0	29.3	55.1	-32.1
2.5	29.7	59.6	-16.9
5	23.4	60.1	-17.0
10	15.3	47.1	-64.1
20	12.9	45.8	-70.0
25	8.95	44.6	-77.1
50	5.73	58.2	-35.2
75	3.51	43.5	-88.5
100	3.05	50.5	-66.3

Supporting Data for Figure 3.4 (d)

Dependence of observed rate constant on solvent composition and dissociating agent at 298.15 K

(d) Dissociation of  $[\text{Co}(\text{Me}_6\text{tren})]^{2+}$  in dimethylsulfoxide by 1.0 M chloroacetic acid in the absence of inert electrolyte: rate constants and activation parameters.

$\% \text{H}_2\text{O}$	$k (\text{s}^{-1})$	$\Delta H^\ddagger (\text{kJ mol}^{-1})$	$\Delta S^\ddagger (\text{J mol}^{-1} \text{deg}^{-1})$
0	9.29	50.6	-56.6
2.5	18.1	61.0	-16.2
5	16.7	66.9	+ 3.00
10	13.5	60.3	-21.0
20	9.52	68.2	+ 2.61
25	8.15	67.3	- 1.70
50	4.11	58.8	-36.0
100	3.56	48.1	-73.1