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PART I - PHOTOCHEMISTRY OF SOME ASYMMETRIC  
COMPLEXES OF RHODIUM, COBALT, AND CHROMIUM.

PART II - A KINETIC STUDY OF THE REACTION OF  
1,10-PHENANTHROLINES AND 2,2'-DIPYRIDYLS WITH  
SQUARE-PLANAR METAL COMPOUNDS.

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AND 2,2'-DIPYRIDYLS WITH SQUARE-PLANAR METAL COMPOUNDS

by

Donald Eugene Schwab

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF CHEMISTRY  
In Partial Fulfillment of the Requirements  
For the Degree of  
DOCTOR OF PHILOSOPHY  
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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my  
direction by Donald E. Schwab  
entitled Part I - Photochemistry of some asymmetric complexes of rhodium,  
cobalt, and chromium. Part II - A kinetic study of the reaction of  
1,10-phenanthrolines and 2,2'-dipyridyle with square-planar metal compounds.  
be accepted as fulfilling the dissertation requirement of the  
degree of Doctor of Philosophy

John V. Pund  
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Date

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*Donald E. Schenk*

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## ABSTRACT

Part I of this dissertation describes the synthesis of various metal complexes. Several of these complexes were partially resolved into optical isomers by a variety of chemical and physical methods. Optically active samples of  $\text{Co}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3$ ,  $\text{K}_3[\text{Cr}(\text{ox})_3]$ , and cis- $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$  (acac = acetylacetonate ion, ox = oxalate ion, and phen = phenanthroline) were irradiated at selected wavelengths. The amount of photoracemization was determined for each sample. These results were compared to thermal racemization and thermal and photochemical decomposition.

The qualitative results are that  $\text{Co}(\text{acac})_3$  photoracemizes slowly at 297, 322, and 595 m $\mu$  at rates in excess of the thermal reaction. Neither photo nor thermal decomposition seriously compete at 25 $^\circ$ , but both do at 55 $^\circ$ .

$\text{Cr}(\text{acac})_3$  slowly photoracemizes at 338 m $\mu$ . No reaction of any kind was detected upon irradiation at 295 or 560 m $\mu$ .

$\text{K}_3[\text{Cr}(\text{ox})_3]$  in a solid KCl matrix undergoes complicated thermal loss of optical rotation. No clear-cut photoracemization was observed.

Cis- $[\text{Rh}(\text{phen})_2\text{Cl}_2]^{+1}$  photoracemizes at moderate rates when irradiated at 273, 336, or 353 m $\mu$  without detectable decomposition. Neither racemization nor decomposition occur in the dark over a period of several days. Rhodium(I) species do not catalyze racemization.

In Part II the reaction of dipyriddy (dipy) with the square-planar complexes,  $\text{K}_2\text{PdCl}_4$  and  $\text{K}_2\text{PtCl}_4$ , was investigated. The reaction

was found to be slow and second order. The effect on the reaction rate was determined when chloride concentration, ionic strength, and pH were varied independently. A parallel path mechanism is proposed which accounts for the observed results. These results are compared to the reactions of these complexes with phen. Dipy reacts more rapidly than does phen with the substrates. It is proposed that phen or dipy reacts with the Pd(II) complex by a dissociative interchange process. This intimate mechanism also describes best the reaction of phen with the Pt(II) complex. When dipy is the ligand the associative interchange process accounts for the result best.

PART I - PHOTOCHEMISTRY OF SOME ASYMMETRIC COMPLEXES  
OF RHODIUM, COBALT, AND CHROMIUM

## CHAPTER 1

### INTRODUCTION

Generation of an optically active system by physical means has been sought for many years. Chemical induction has been used by organic chemists. However, their attempts have been indirect methods; they require pre-existing enantiomers to generate new ones. Biological generation of active systems has been known since the time of Pasteur, when living organisms were employed to resolve racemic mixtures. Again this method requires use of pre-existing asymmetric agents. A physical technique to accomplish resolution has been recognized on theoretical grounds for many years. Each optical isomer of a racemate has a different absorption coefficient for circularly polarized light. If a racemic mixture is irradiated by such light, one of the optical isomers should absorb light and become activated for chemical reaction. If the chemical reaction is racemization, the more activated isomer will become depleted while the less activated portion will accumulate. The net effect of this process is resolution of the racemate.

The compound  $K_3[Co(ox)_3]$  has been subjected to these conditions. Jaeger and Berger (1921) failed to verify the supposition under varied experimental conditions. Partial resolution was reported by Tsuchida, Nakamura, and Kobayashi (1935) but their claim has been accepted with reservation (Kauffman, Takahasi, and Sugisaka 1966).

Biological systems include a vast number of complex molecules. Asymmetry of biological molecules allows discrimination in their reactivity. Metal ions are involved in specific ways with many biological reactions. The particular geometric interaction of metal ions and biochemical compounds is of interest, although largely unknown.

Amino acids isolated from proteins have the L-configuration. Chemical synthesis produces both isomers equally; why, then, is only one found in natural systems? One explanation is that both optical isomers were made, but one of them was destroyed by a process similar to that suggested above. Chemical induction of all subsequent molecular synthesis could perpetuate the isomeric purity of these compounds.

Coordination compounds can be used as a model system for the investigation of these areas. The complexes must meet the conditions:

1. In order to undergo racemization, the compound must be resolved into optical isomers. Only tetrahedral and octahedral complexes are useful if we insist that the optical isomerism exists about the metal ion itself and not be due to ligands.

2. The complex must absorb light in an accessible region of the spectrum. Information about the differential effect of light absorption in the d-d, charge-transfer, and ligand bands is desirable. Some transition metal ions possess the necessary properties.

Tetrahedral metal complexes are numerous but form enantiomers only when coordination is to four dissimilar uni-dentate ligands or two unsymmetrical bidentate ligands. Unfortunately tetrahedral complexes are usually too labile to be resolved (Dwyer and Mellor 1964).

Many octahedral complexes of transition metals are asymmetric. The inert  $d^3$ ,  $d^6$ , and  $d^8$  metal ions are inert toward resolving conditions but labile enough that isomerization may take place.

Upon absorption of light a molecule is promoted to an excited electronic state. Energy must be dissipated by the molecule in one of several ways before it returns to the ground state. Internal conversion, intersystem crossing, photoluminescence, and intermolecular energy transfer do not lead directly to chemical reaction. Chemical reaction from the excited state may compete with these decay processes if relaxation is slow. Oxidation-reduction, substitution, and isomerization are the three possible reactions which may take place. More than one of these may occur simultaneously.

Redox reactions are likely when the absorption causes an electron to be transferred from one part of the complex to another. This process is called charge transfer and irradiation at the charge transfer energy leads to extensive redox. Usually the metal ion is reduced at the expense of a ligand or solvent molecule. A very useful example of this reaction is the ferrioxalate actinometer system where Fe(III) is reduced, while one of the three oxalate ligands is oxidized to carbon dioxide. The primary photochemical process for redox is thought to be homolytic fission of the metal-ligand bond (Adamson and Sporer 1958).

Substitution reactions are a common consequence when metal carbonyls are excited. Either substitution by a strong Lewis base or disproportionation to form substituted ionic metal carbonylates occurs (Strohmeir 1964). Aquation is a common process when coordination

compounds are irradiated in aqueous solution. It is difficult to avoid this reaction regardless of the irradiating energy, and irradiation at the d-d band increases the aquation quantum yield. An interesting feature of aquation is that generally only complexes which are susceptible to thermal aquation are found to be photochemically active. In addition, the photorate is frequently faster than the thermal rate (Wehry 1967).

Isomerization like substitution is only important when the complex undergoes thermal rearrangement and usually only when photosubstitution also takes place (Wehry 1967). Isomerization may be either cis-trans isomerization or racemization.

Photoracemization studies of coordination compounds are limited (see review, Adamson 1968). All reported complexes have been octahedral and contained chelating ligands. Oxalate complexes have been the most extensively studied; only four different metal ions have been cited: Cr(III), Rh(III), Co(III), and Ni(II).

In the visible region  $\text{Cr}(\text{ox})_3^{-3}$  ion photoracemizes through an aquation of one ligand site ( $E_a = 15.0$  Kcal/mole, quantum yield about 0.1 and nearly independent of wavelength). No other process was observed. Photoexchange of  $^{18}\text{O}$  with solvent oxygen demonstrated that the twist mechanism was not involved (Spees and Adamson 1962). The rate of photoracemization is pH dependent, which supports carboxylate dissociation as the primary event. Free oxalate does not appear during the reaction. Slight solvent dependence occurs, and the reaction rate



increases slightly in organic solvents. Photoracemization has not been reported for other chromium complexes.

Four rhodium complexes are known to photoracemize. Dwyer and Garvan (1960a, 1961) reported that  $\text{Rh}(\text{H}_2\text{O})(\text{EDTA})^{-1}$  and  $\text{Rh}(\text{H}_2\text{O})(1\text{-PDTA})^{-1}$  mutarotate if exposed to light. Both complexes regained full optical activity if placed in the dark. It was postulated that the symmetry of the complex is reduced by dissociation of a carboxyl group followed by reversible aquation. The process is fully reversible because the free carboxylate group is confined near its original coordination site. The Co(III) and Cr(III) complexes fail to racemize under the same conditions (Dwyer, Gyarfas, and Mellor 1955). The ion  $\text{Rh}(\text{ox})_3^{-3}$  racemizes and decomposes when irradiated at 546 m $\mu$  (Spees and Adamson 1962). The compound  $\text{Rh}(\text{phen})_2\text{Cl}_2^{+1}$  photoracemizes when irradiated at any of the three major absorption maxima (352, 336, and 273 m $\mu$ ) (Schwab and Rund 1970).

Several cobalt(III) complexes have been examined which contain oxalate. The series  $\text{Co}(\text{ox})_3^{-3}$ ,  $\text{Co}(\text{ox})_2(\text{en})^{-1}$ , and  $\text{Co}(\text{ox})(\text{en}_2)^{+1}$  is progressively more stable toward photoracemization (and decomposition as well); the last example is completely stable (Dwyer, Reid, and Garvan 1961; Spees and Adamson 1962; Bushra and Johnson 1939). These results included aqueous solution and solid state irradiation. The series  $\text{Cr}(\text{ox})_3^{-3}$ ,  $\text{Rh}(\text{ox})_3^{-3}$ , and  $\text{Co}(\text{ox})_3^{-3}$  shows increased lability with respect to photoracemization. It should be noted that loss of optical rotation of  $\text{Co}(\text{ox})_3^{-3}$  is due to direct isomerization (15%) and to extensive photoreduction (85%) of the complex. It may be, then, that the

cobalt and rhodium compounds actually racemize with nearly the same facility (Spees and Adamson 1962).

The complex ion d or l-cis- $[\text{Co}(\text{en})_2(\text{Cl})_2]^{+1}$  stereospecifically aquates one chloride to form d or l-cis- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{Cl})]^{+2}$ . Two groups have reported photoracemization of the aquo species. Additional aquation also occurred, and it is not clear whether the loss of optical activity is due to direct racemization or via the aquation reaction (Spees and Adamson 1962; Moggi, Sabbatine, and Balzani 1967). Moggi's group reported quantum yields for racemization: 0.0035 at 600 m $\mu$ , and 0.07 at both 313 and 254 m $\mu$ .

A nickel(II) complex,  $\text{Ni}(\text{phen})_3^{+2}$  photoracemized in aqueous solution at about twice the rate when irradiated as during the dark reaction (Rund 1970b).

Before the photoresolution of a racemate can be studied, the reverse process (photoracemization) must be analyzed. The study may use nonpolarized irradiation but should investigate wavelength dependence. The competitive reactions, including racemization, will occur simultaneously. The resolution rate must be corrected for all side reactions. Consequently the complicating side reactions must be identified and their magnitudes determined.

Two things can be done to reduce competition by solvolysis. First, noncomplexing solvents can be used. The number of complexes which are soluble in inert solvents are few, but benzene will dissolve some complexes and display photo inertness. Secondly, samples can be made using an inert solid support such as an alkali halide pellet.

## CHAPTER 2

### EXPERIMENTAL

#### Synthesis

The following compounds were made by the literature methods:  $K_3[Fe(C_2O_4)_3] \cdot H_2O$  (Hatchard and Parker 1956),  $K[Cr(C_2O_4)_3] \cdot xH_2O$  (Bailar and Jones 1939),  $K[Cr(NH_3)_2(NCS)_4]$  (Wegner and Adamson 1966),  $Co(glycine)_3$  (Volshtein 1952),  $Cr(biguanidine)_3$  and  $Cr(biguanidine)_3 \cdot HCl$  (Ray 1960),  $Na_3[Co(NO_2)_6]$  (Brauer 1965),  $Na[Co(acac)_2(NO_2)_2]$  and cis- $[Co(acac)_2(NH_3)_2]I$  (Cotsoradis and Archer 1967, Archer and Cotsoradis 1965, Boucher and Bailar 1965),  $Rh(acac)_3$  (Dwyer and Sargeson 1953),  $Co(acac)_3$  (Bryant and Fernelius 1957),  $Cr(acac)_3$  (Fernelius and Blanch 1957),  $Fe(oxine)_3$ ,  $Co(oxine)_3$ , and  $Cr(oxine)_3$  (Ablov 1933). The synthesis of  $[Rh(phen)_2Cl_2]Cl \cdot 3H_2O$  was based on Gillard and Heaton's method (1969) and is reported in detail elsewhere (Schwab and Rund 1970).

Two methods were used to synthesize  $Cr(glycine)_3$ :

1. Volshtein's (1952) procedure for the preparation of  $Co(glycine)_3$  was adapted to the chromium complex. Glycine (13.5 g, 0.15 moles) and  $CrCl_3 \cdot 6H_2O$  (16.0 g, 0.06 moles) were dissolved in 500 ml of water and warmed to about  $90^\circ$  for 4 hours. The green solution became purple over that period. A solution of KOH was added until the pH = 10 according to indicator paper. In a few minutes a gray ppt formed; the mixture was allowed to stand overnight and the gray ppt

was removed by suction filtration. The product, a pink solid, pptd from the filtrate upon standing for several days at room temperature.

2. The method of Ley (Ley and Ficken 1912, Ley and Winkler 1902) was used to prepare alpha(trans-1,2,6) and beta(cis-1,2,3) Cr(glycine)<sub>3</sub>.

### Resolution of Optical Isomers

#### Chromatography

Neutral Complexes. Racemic mixtures of the neutral complexes Co(acac)<sub>3</sub>, Cr(acac)<sub>3</sub>, and Rh(acac)<sub>3</sub> were partially resolved by chromatography as previously reported (Moeller and Guylas 1958, Collman et al. 1963). Commercial lactose (Mallinckrodt) was used without further preparation as the stationary phase. A 1.0 g portion of the complex was applied to the column in 30 ml of benzene-heptane (1/3 vol) solvent. A flow rate of about 1 ml/min produced breakthrough after 40-50 hours. The complex was collected as a total effluent of 200-300 ml (50 ml fractions). Repeated chromatography produced no further resolution. The optical rotation of the effluent was measured at either the mercury line (545 mμ) or the sodium D line (590 mμ), whichever showed the larger value (590 mμ for Co and Cr and 545 mμ for Rh). The concentration of each solution was measured spectrophotometrically [Co(acac)<sub>3</sub>: ε = 450 ml/g-cm at 595 mμ, Cr(acac)<sub>3</sub>: ε = 200 ml/g-cm at 561 mμ].

Cationic Complexes. Cis-[Co(acac)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]I was partially resolved by the method of Legg and Douglas (1967). A cation exchange cellulose (Cellex-CM, BioRad Laboratories) in the sodium form was used as the stationary phase after being washed, slurried, packed, and

washed once again with 0.01 M  $\text{NaClO}_4$ . The column was washed with water before the complex (0.1 g in 15 ml of water) was applied to the column and eluted with the perchlorate solution. Eight fractions of about 1-15 ml each were collected over 1½ hours, and rotation,  $\alpha_{545}$ , was determined. The concentration was measured spectrophotometrically ( $\epsilon = 268 \text{ ml/g-cm}$  at 546 m $\mu$ ). The specific rotations calculated ( $25^\circ$ ,  $\text{H}_2\text{O}$ ) ranged from +134 degree-ml/g-cm for fraction #2 to -102 degree-ml/g-cm for the last fraction eluted from the column.

The above conditions were also applied to  $[\text{Cr}(\text{bigH})_3]\text{Cl}_3$ . The yellow-orange band of complex was not observed to elute from the column but did form a band of perceptibly darker color. Washing with water, 0.01 M  $\text{NaClO}_4$  or dilute HCl failed to move the band.

Likewise,  $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}\cdot 3\text{H}_2\text{O}$  was resolved by the same method except that the column was fitted with a water jacket and cooled to  $5^\circ$ . Breakthrough occurred after 3 hours. This is the first time this complex has been resolved although Gillard and Heaton (1969) tried unsuccessfully to resolve diastereoisomers of the cation. The ORD curve has been published elsewhere (Schwab and Rund 1970).

#### Diastereoisomer Formation

Cis- $[\text{Co}(\text{acac})_2(\text{NH}_3)_2]\text{I}$ . Four procedures failed to resolve a racemate of this complex. Three methods using d-tartrate and one using d- $\alpha$ -bromocamphor- $\pi$ -sulfonate were attempted:

1. Sodium tartrate: A saturated aqueous solution of Na-d-tartrate (Mallinckrodt Chemical Works) was used to dissolve the solid racemate, resulting in a pale red-pink solution. No ppt formed. The

solution was extracted with chloroform to remove any diastereoisomer formed. Both phases contained some of the original color. An optical rotatory dispersion (ORD) spectrum of the organic phase revealed no rotation between 650 and 300 m $\mu$ . The aqueous phase gave ORD curve of different shape than pure resolving agent, but no solid could be isolated short of complete evaporation of the solution.

2. Silver d-tartrate: This resolving agent was prepared by the procedure of Busch (1955) and used immediately. A 1:1 mole mixture of the two compounds was made by adding 70 mg of solid tartrate salt to 15 ml of aqueous solution of the complex (100 mg) and the suspension was stirred for 30 minutes. The color changed from orange to violet. The white solid was removed by suction filtration, washed with water, and discarded. The concentrated filtrate failed to yield a useful ppt after the addition of an equal volume of EtOH. Only a small amount of black, insoluble solid was isolated.

3. Antimony potassium d-tartrate,  $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$  (Fisher Scientific Company): Dwyer and Garvan (1960b) resolved cis- $[Co(en)_2(NO_2)_2]NO_2$  using this agent. The first "diastereoisomer" isolated was converted to the iodide by adding NaI to the aqueous solution of the isomer. The ppt which immediately formed was collected, dried, and dissolved in chloroform. This solution displayed no rotation between 600 and 500 m $\mu$ . An aqueous solution of the other "diastereoisomer" was treated with KBr; the resulting ppt was collected, dried, and finally dissolved in chloroform. Again no rotation was observed over the same wavelength region.

4. Ammonium d- $\alpha$ -bromocamphor- $\pi$ -sulfonate: This reagent has been used to resolve cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl (Bailar 1946). When used with the current complex no solid was obtained. The resolving agent was recovered in large yield from the crude reaction mixture.

The results were the same when Cr(big)<sub>3</sub> was treated with either (a) silver d-tartrate (as described above) or (b) d-tartaric acid (Ray and Dutt 1941). The dd and dl diastereoisomers formed were separated after tituration. Crystallization of either diastereoisomer from aqueous solution proved impossible, and the solids were pptd by the addition of ethanol. Both diastereoisomers gave the same ORD curve over the range 650-280 m $\mu$ . The diastereoisomers were not converted to the enantiomers.

The procedure of Werner (1912) as given by Johnson and Mead (1935a,b) was used to resolve K<sub>3</sub>[Cr(ox)<sub>3</sub>] $\cdot$ xH<sub>2</sub>O. The ion d-Cr(ox)<sub>3</sub><sup>-3</sup> racemizes rapidly in aqueous solution. When the pure enantiomorph is freed from its strychnine salt, all manipulations must be carried out rapidly and at 0°. Results are improved further if the mixture is filtered into a flask containing ethanol, rather than adding alcohol to the filtrate. All of these modifications force the free potassium salt to ppt more quickly.

### Irradiation System

#### Solution Samples

Irradiation Equipment. Figure 1 is a diagram of the apparatus used to irradiate samples. The system allows variation of wavelength,

diameter of light beam and sample temperature. All components could be adjusted independently for horizontal and vertical position. The components of the irradiation system shown in Figure 1 are:

- a. Power supply; Hanovia 1000 watt power system with high voltage starting circuit.
- b. Lamp housing; Schoeffel Instrument Company, #LN 151N with cooling fan.
- c. Lamp; Hanovia, #538C, 900 watt high pressure, compact xenon filled.
- d. Quartz lens; adjustable focus (supplied with housing).
- e. Dichroic mirror; Bausch and Lomb, heat control filter #45-8, heat transmitting/visible reflecting,  $45^{\circ}$  incidence; cut off approximately 650 m $\mu$ .
- f. Cooling block; brass block, black first surface; cooled by a circulating water supply.
- g. Diaphragm; circular orifice, variable opening diameter.
- h. Blocking filter; Corning Glass Works, glass color filters, broad window or cut off type (available from Tinsley Laboratories, 2448 6th Street, Berkeley, California 94710).
- i. Lens; double convex quartz, 63 mm focal length.
- j. Lens; double convex quartz, 87 mm focal length.
- k. Filter; narrow pass, interference type.
- l. Sample cell holder and constant temperature block; brass, cooled by thermostated circulating water.



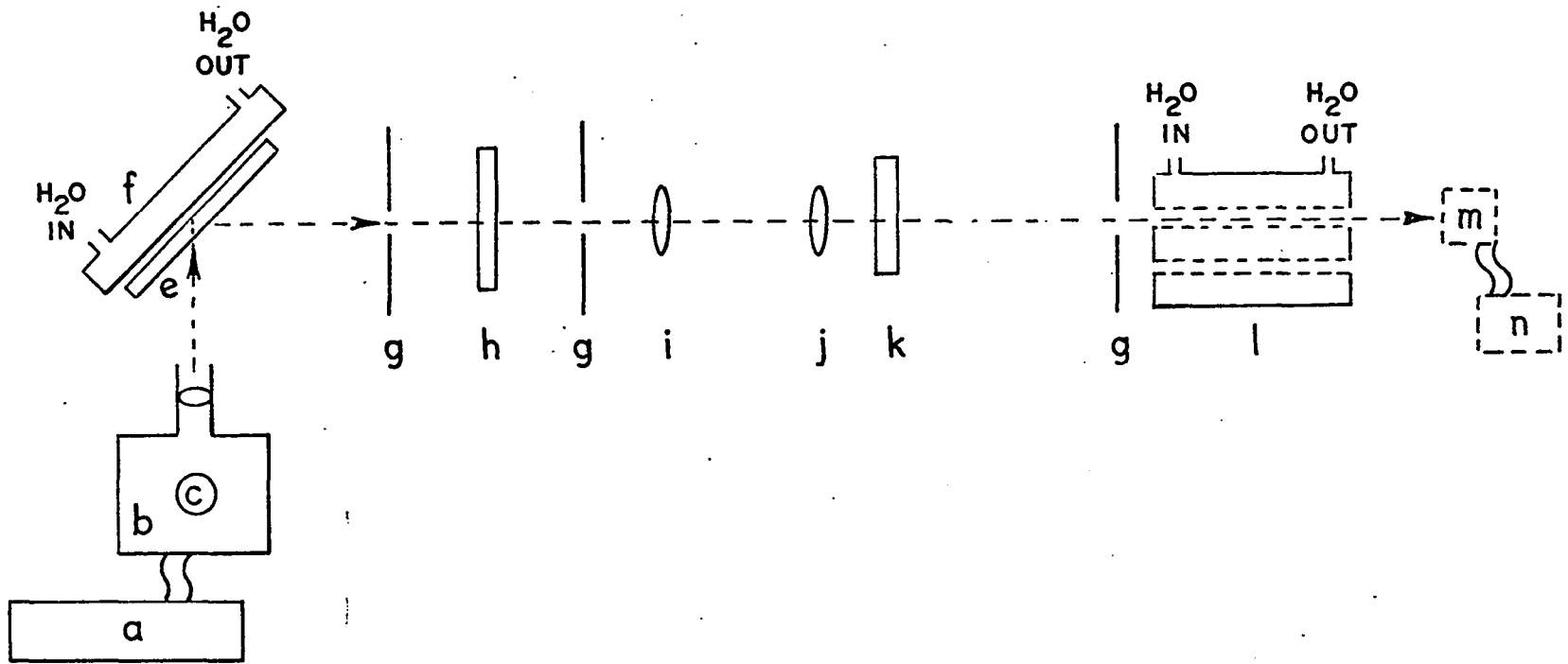


Figure 1. Irradiation system.

m. Thermopile; Kipp (Holland), #E1 5379.

n. Microvolt meter; Keithley Instruments, #150A microvoltmeter.

The xenon lamp generates a small, intense arc of continuous wavelength energy from 290  $\mu$  into the infrared. The light emerges from the lamp housing through the lens and is reflected  $90^\circ$ , while the heat and infrared irradiation is transmitted through the dichroic mirror and absorbed by the cooling plate. The first two diaphragms are adjusted to minimize stray light, the two lens (i and j) collimate the beam to a nearly parallel path and the final diaphragm controls the diameter of the beam so that it just fills the sample cell without contacting the cell walls. The blocking filter (h) reduces the beam to a broad window of wavelengths, protects the delicate interference filter from heat and blocks the secondary windows of the interference filters. The interference filter passes only a narrow band of light (as narrow as 13  $\mu$  at half height). Unfortunately only 10-15% of the incident intensity is passed.

Temperature control of the sample was maintained by circulating thermostated water ( $\pm 0.1^\circ$ ) through the cell holder. Cylindrical (22 mm O.D.) Cary spectrophotometer cells were used as sample containers. The cells were placed in two parallel holes (23 mm I.D.) in the cell holder. One cell is placed in the beam and the other is consequently in the adjacent nonirradiated position. The sample concentration or cell length was selected so that the sample completely absorbed the light beam. Sealed

cells were necessary to prevent slow evaporation of solvent; ground stoppered cells were satisfactory for irradiations of only several days.

### Solid Samples

Irradiation Equipment. Solid samples were irradiated by the analyzing beam in a Cary 60 spectropolarimeter. During a photo run the polarimeter continuously recorded the rotation at the selected wavelength. The thermal reaction was run under identical conditions with the analyzing beam slit closed.

The samples were prepared in the same manner as pellet samples for infrared spectroscopy. A transparent disc 1 mm x 13.5 mm was produced by 8 tons pressure when the matrix material was 200 mg of KBr; KCl required 11 tons pressure.

### Actinometry

Of the several techniques available to determine light intensities, two were used. The ferrioxalate actinometer of Hatchard and Parker (Parker 1953, Hatchard and Parker 1956, Parker and Hatchard 1959, and Lee and Seliger 1964) was used for wavelengths shorter than 400 m $\mu$  and a thermopile at lower energies. The thermopile was calibrated against the ferrioxalate system for each determination.

The ferrioxalate system was used as given, except a x5 amount of phenanthroline was needed to develop the samples fully. The composition of the developing solution was adjusted to accommodate the low solubility of phenanthroline in water. The final solution contained: 3 ml of ferrous containing sample, 3 ml of 0.1% phenanthroline and 1.5 ml of

buffer. A 30-minute development time prior to reading the absorbance at 510 m $\mu$  was satisfactory. The actinometer solution in a 1.0 cm quartz windowed cell was placed in the irradiating beam for sufficient time to produce an absorbance of the developed solution of 0.2-1.0. Each ferrioxalate solution was checked at the irradiation wavelength to insure that it would absorb 99+% of the light passing into it.

#### Kinetic Parameters

The concentration of the experimental solutions were determined spectrophotometrically using either a Beckman DU or a Cary 14 spectrophotometer.

The molecular rotation was calculated from the expression:

$$[M] = \frac{[\alpha] \times 100}{M.W.}$$

The specific rotation was calculated from the observed rotation using the expression:

$$[\alpha] = \frac{\alpha_{obs}}{l \times conc}$$

where  $l$  is the path length of the sample in decimeters, the concentration of the sample is in gm/ml, and the rotation measured in degrees.

Since the degree of resolution of complexes is unknown, the initial concentration of a particular isomer is also unknown. As is customary the quantum yield is defined in this case as: reaction rate constant/irradiation rate. The quantum yield then has the units of einsteins-sec<sup>-2</sup> for first-order racemizations.

The usual rate law was used. The first order rate constant was obtained from the slope of the plot:  $\log (\alpha_{\text{obs}})$  vs time.

## CHAPTER 3

### RESULTS

Of the metal complexes described in the experimental section, only six were resolved to a usable extent. These were:  $\text{Co}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3$ ,  $\text{Rh}(\text{acac})_3$ , cis- $[\text{Co}(\text{acac})_2(\text{NH}_3)_2]\text{I}$ ,  $\text{K}_3[\text{Cr}(\text{ox})_3]$ , and cis- $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$ . The remaining compounds failed to respond to resolution procedures for a variety of reasons. The most common difficulty was the preparation of diastereoisomers. The racemate or resolving salt was often the least soluble salt in the solution; these crystallized from the solution before the desired diastereoisomer. A second problem was that several of the complexes were insoluble in benzene. No attempt was made to resolve these compounds.

The six complexes were resolved only partially. The neutral coordination compounds resolved by chromatography on the lactose column showed lower specific rotation than Collman et al. (1963) obtained. Increased rotation was not achieved when fractions were rechromatographed.

#### Experimental Difficulties

The complexes  $\text{Co}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3$ ,  $\text{K}_3[\text{Cr}(\text{ox})_3]$ , and cis- $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$  were irradiated. Reproducible results were obtained for none of them. Irradiation by circularly polarized light was not undertaken.

Reasons for the nonreproducible results are experimental in nature. The most serious difficulty for the solution samples was the small rotation observed. Observed rotations of only several thousandths of a degree allowed normally small, random errors to become serious effects.

Three additional general areas can be identified as sources of experimental difficulty, the first being the uncertainty of the quantum yield determination at long wavelengths. It was necessary to use a thermopile at low energy where the chemical actinometer absorbs too little light to be effective. Each chemical actinometry run gives intensity values of only about 10% precision. In the low energy region, the light intensity is known to about 15%. It was hoped that the need for the thermopile could be avoided. Adamson (Wegner and Adamson 1966) developed the chemical actinometer,  $K[Cr(NH_3)_2(NCS)_4]$ , for use in the visible region. Unfortunately it could not be recrystallized without decomposition.

Secondly, the lamp intensity decreased nonlinearly with time. The solution systems underwent photoracemization slowly; over a period of several weeks only 10% to 15% of the observed rotation disappeared. Declining light intensity poses a serious problem on this time scale when quantum yields are calculated.

The third area of difficulty was measurement of the rotation of the samples. The response of the polarimeter was sensitive to the precise position of the sample cell. This problem was minimized but not

completely eliminated. The small values of the rotation magnify this source of error.

The solid samples of  $K_3[Cr(ox)_3]$  present problems primarily due to nonuniform sample conditions. Since the samples were prepared by the application of high pressure to form pellets, there may follow a relaxation process within the structure of the disc. The amount of moisture in the disc or the particle size of the chromium complex may also vary from pellet to pellet.

#### Irradiation of Resolved Complexes

##### Co(acac)<sub>3</sub>

The results of irradiation of  $Co(acac)_3$  in 1:1 (vol) benzene/heptane solvent are collected in Table 1. The photorates shown are the observed rates corrected for thermal racemization and photodecomposition. Decomposition was followed by the decrease in absorbance at 595 m $\mu$  and the rate constants are listed for both thermal and photo samples. The nonreproducibility of data restricts them to qualitative value only. A typical kinetic plot is shown in Figure 2.

The results for 297 m $\mu$  indicate decomposition was not affected by photolysis but racemization was accelerated slightly. Photoracemization is the predominant process.

At 322 m $\mu$  the quantum yield for racemization exceeds that for decomposition, although the magnitude of the difference is hard to estimate. There seems to be little increase with respect to the 297 m $\mu$  sample. Qualitatively the photo reactions are faster than the thermal ones for both decomposition and racemization.



Table 1. Results of irradiation of  $\text{Co}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$ .

$\lambda$ , m $\mu$	$I_{\text{absorbed}}$ $\times 10^6 \text{ E min}^{-1}$	$k$ , thermal $\times 10^6 \text{ min}^{-1}$	$k$ , photo $\times 10^6 \text{ min}^{-1}$	$\Phi = \frac{k_d}{k_I}$	$k$ , thermal $\times 10^6 \text{ min}^{-1}$	$k$ , photo $\times 10^6 \text{ min}^{-1}$	$\Phi = \frac{k_r}{k_I}$	Total time, min
<u><math>\text{Co}(\text{acac})_3</math></u>								
297 <sup>a</sup>	2.54±0.6	1.0±0.5	0.5±0.5	0.20±0.04	-	5.8±4.2	2.3±4.0	25,000
322	8.88±1.08	0.1±0.5	1.9±0.1	0.22±1.0	0.02±0.02	3.6±0.7	0.4±0.7	50,000 <sup>c</sup>
322	not measured	0.5±0.6	5.0±1.6	-	0.2 ±1.0	78±50	-	24,000
322	7.5±0.6	1.0±1.0	3.2±1.0	0.43±0.8	-	27±27	3.6±0.7	10,000
322 <sup>b</sup>	2.88±0.26	3.6±2.5	4.2±2.8	1.5±2.8	8±2	18.5±5.2	6.5±1.7	25,000
595	53.1±4.0	1.9±0.9	1.6±0.4	0.03±4.0	-	6±3	0.1±1.7	25,000
<u><math>\text{Cr}(\text{acac})_3</math></u>								
295	1.12±0.3	0	0	-	0	0	-	5,000
338	26.1±1.6	1.1±0.4	1.4±0.6	0.09±1.5	0.7±0.7	16±1	0.6±0.7	35,000
560	not measured	0	0	-	0	0	-	6,000

a. Temp = 25° unless indicated otherwise

b. Temp = 55°

c.  $k = 0$  for racemization during the first 18,000 min; data shown is for the subsequent 50,000 min.

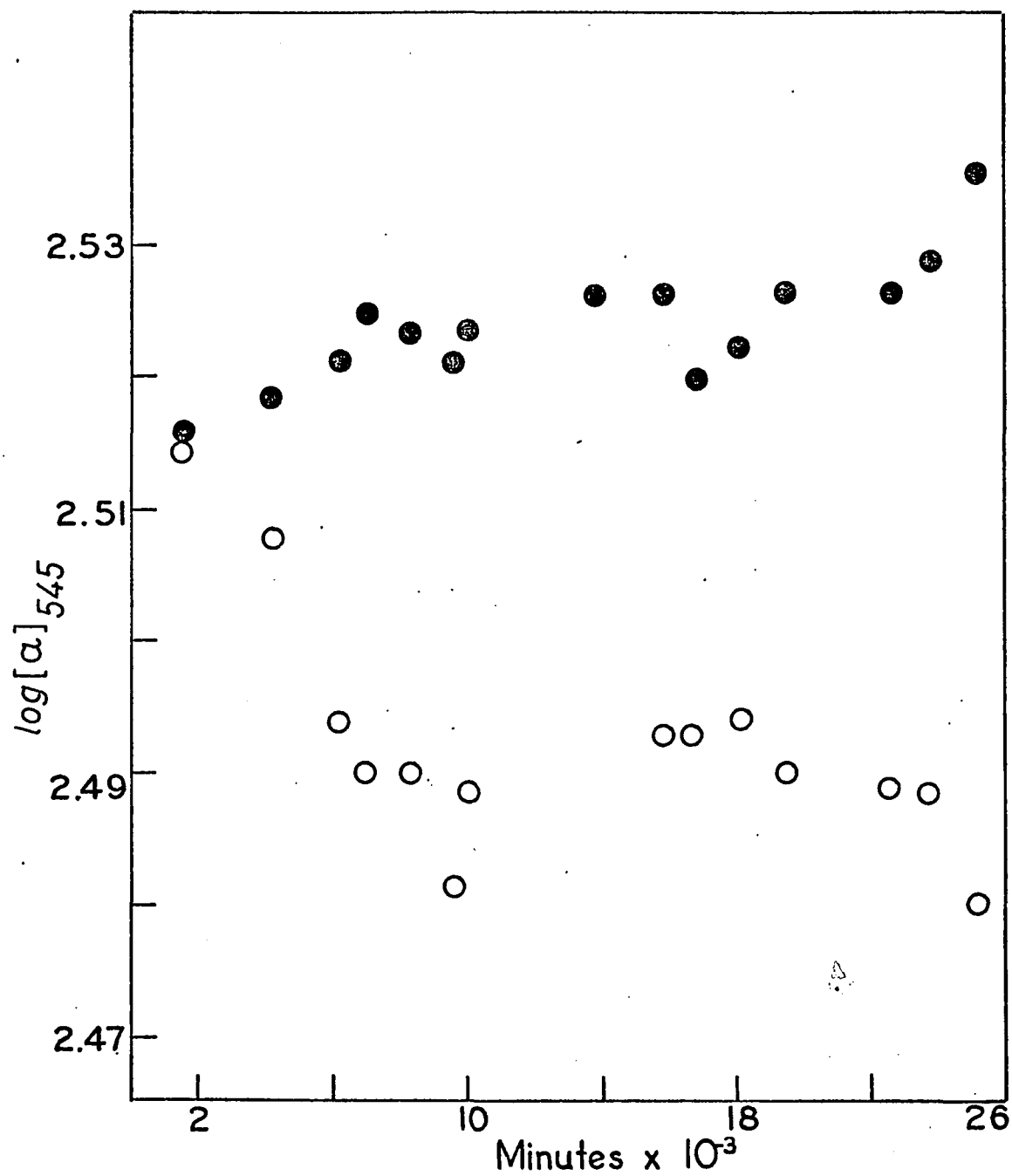


Figure 2. Sample plot. Irradiation of  $\text{Co}(\text{acac})_3$  at 295 mμ.

First entry in Table 1; ○ photo, ● thermal.

Decomposition again is not increased when  $\text{Co}(\text{acac})_3$  is irradiated at 595 m $\mu$ , while racemization is accelerated. Photoracemization is once more the major reaction.

Generally for cobalt complexes the quantum yields are strongly wavelength dependent and increase with the energy of irradiation (Spees and Adamson 1962). This is not true in the current case for either decomposition or isomerization. Racemization is the major result of photolysis and is not the result of decomposition. Spees and Adamson (1962) found that in aqueous solution  $\text{Co}(\text{ox})_3^{-3}$  undergoes excellent first-order photoracemization. However, comparison of the quantum yields for substitution and isomerization revealed that 85% of the racemization was a consequence of aquation.

At 55° thermal racemization is no longer a small contribution to the total loss of rotation and now accounts for about 30% of the total reaction. Likewise both thermal and photodecomposition have become serious competitors to photoracemization.

### $\text{Cr}(\text{acac})_3$

No reaction of any kind was observed when irradiation was at either 295 or 560 m $\mu$ . The results at 338 m $\mu$  show a small amount of decomposition but no acceleration caused by photolysis. The data in Table 1 show that the loss of optical rotation is primarily due to isomerization, not decomposition. Figure 3 shows the change in rotation vs time.

Other reports compare chromium and cobalt complexes. Chromium(III) showed decreased importance of photodecomposition with

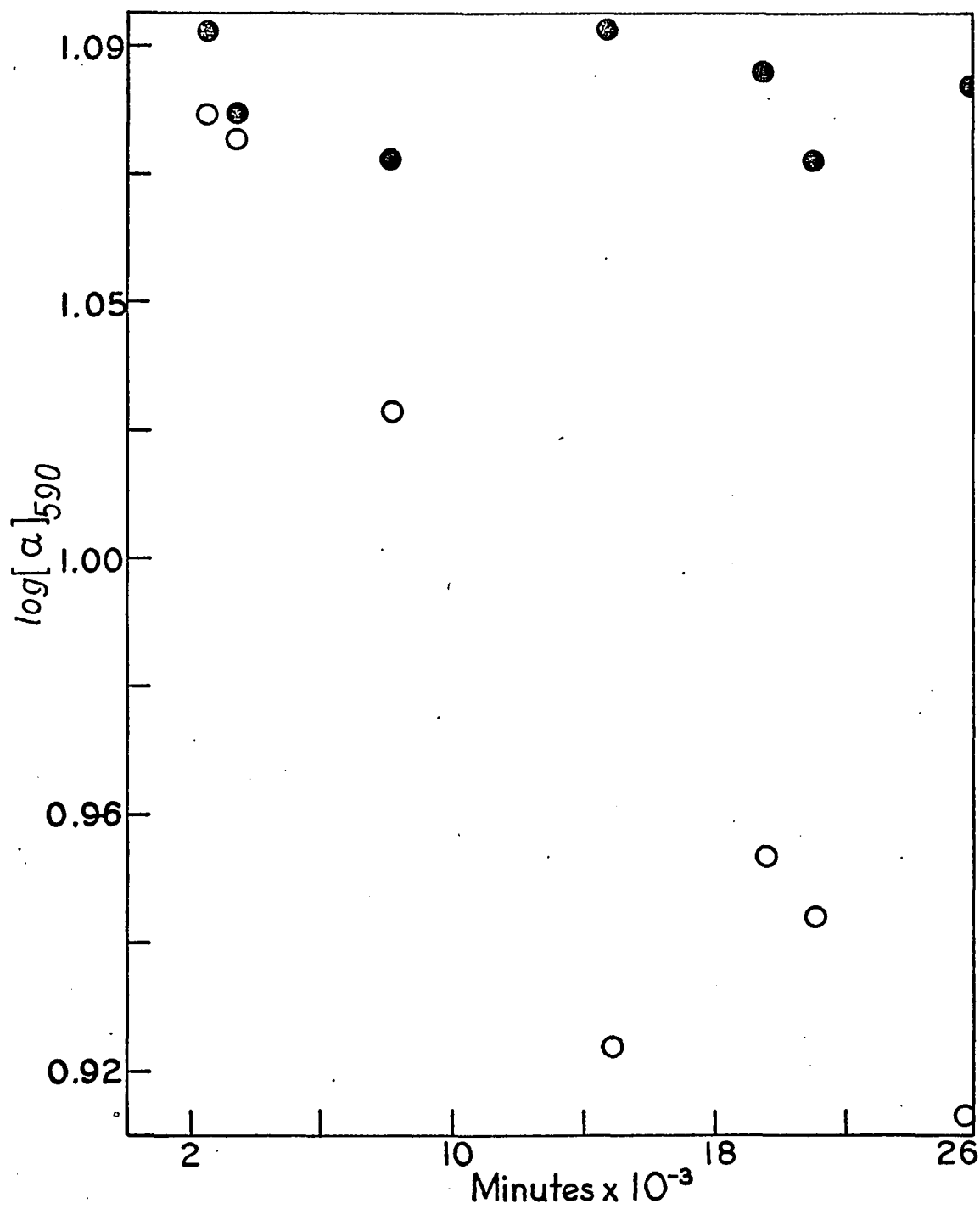


Figure 3. Sample plot. Irradiation of  $\text{Cr}(\text{acac})_3$  at 338 m $\mu$ .  
Eighth entry in Table 2;  $\circ$  photo,  $\bullet$  thermal.

respect to other processes (Wehry 1967). This generalization is not verified here. This is a consequence of the noncoordinating solvent system in the present work failing to provide a reducing source for the cobalt(III) complex.

### K<sub>3</sub>[Cr(ox)<sub>3</sub>]

The photo reaction of a complex in a solid matrix was followed using K<sub>3</sub>-d-[Cr(ox)<sub>3</sub>] in KCl. As indicated in Table 2, several photo and thermal runs were done using the same sample disc before it was discarded. A typical plot is shown in Figure 4. The rate constant for any spot on the disc (isolated by a cardboard mask) became smaller from one experiment to the next, regardless of prior history. The thermal processes are complicated and loss of observed rotation is not a simple first-order function. This is probably the dehydration phenomenon reported by Johnson and Mead (1935a,b). The rate constants for the thermal racemization vary over the range  $0.7 \times 10^{-5} \text{ min}^{-1}$  to  $50 \times 10^{-5} \text{ min}^{-1}$ . With one exception the photorate constants are of the same order of magnitude, e.g., about  $5 \times 10^{-5} \text{ min}^{-1}$ .

Because of the experimental conditions required by the solid samples, no determination of the change in concentration could be made. No attempt was made to measure quantum yields.

### Cis-[Rh(phen)<sub>2</sub>Cl<sub>2</sub>]Cl

A solution of d-cis-[Rh(phen)<sub>2</sub>Cl<sub>2</sub>]<sup>+1</sup> in 0.01 M NaClO<sub>4</sub> showed no decrease in either the observed rotation at 353 mμ or the absorbance at 273, 336, and 352 mμ upon standing in the dark over a period of 48 hours.

Table 2. Results of irradiation of  $K_3[Cr(ox)_3]$ .

Disc No.	$\mu$	k, thermal $\times 10^5 \text{ min}^{-1}$	k, photo $\times 10^5 \text{ min}^{-1}$ <sup>a</sup>	Total min	Remarks <sup>b</sup>
1a	571	50±10	-	1300	New disc aged one day before use.
b	571	30±24	-	2000	
c	571	-	6.5±0.2	2800	
d	417	-	7.4±3	1630	
e	417	-	14±6	450	New spot on disc.
f	698	-	0	1500	
g	571	0	-	840	
h	571	10±9	-	1300	
i	571	-	2.0±1.3	2500	
2a	571	21±7	-	1400	New disc used immediately upon preparation.
b	571	-	3.0±0.2	1200	
c	571	0.73±0.1	-	3800	
3a	571	-	4.5±1.0	3900	New disc stored 3 wks in desiccator before runs a, b.
b	571	1.2±0.1	-	6000	
4a	571	-	11	3500	New disc aged 8 hours before run.
b	571	4.7±1.9	-	3000	
c	571	-	1.2±0.4	1800	
d	571	-	0.6±0.2	2500	Same disc as 4a, b, c, but 11 days later. Stored in desiccator.

a. Photo rate constants not corrected for thermal reaction.

b. Slit = 0.20 mm except at 698  $\mu$  was 0.10 mm.

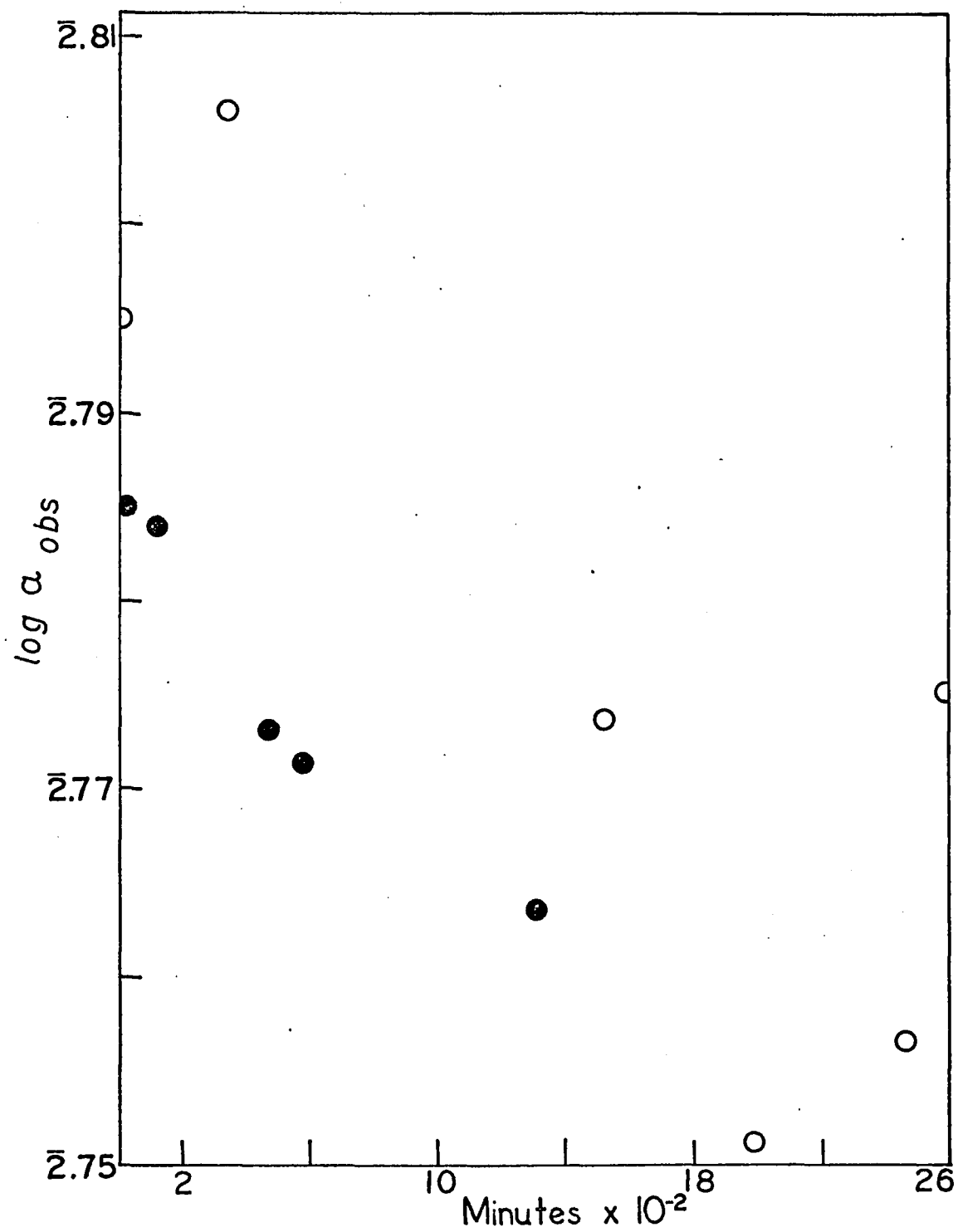


Figure 4. Sample plot. Irradiation of  $K_3[Cr(ox)_3]$  at 571 m $\mu$ .

Taken from Table 2 entries;  $\circ$  photo (disc No. 1c),  $\bullet$  thermal (disc No. 1a).

On the other hand, when a similar sample was irradiated in the polarimeter at 273 m $\mu$  the observed rotation decreased from  $14.8 \times 10^{-3}$  degrees to  $8.4 \times 10^{-3}$  degrees in 300 minutes. A linear plot of  $\log(\alpha_{273})$  versus time showed this was the result of racemization, not decomposition. Parallel results occurred at 336 and 353 m $\mu$ . The results are summarized in Table 3. Figure 5 shows these results.

Gillard and Heaton (1969) have remarked that racemization may be catalyzed by a rhodium(I) species. Added  $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ , a known catalyst for rhodium(III) reactions (Rund 1968), induced no loss of rotation in the dark when present in the amount of 10% Rh(I) per Rh(III). When added in manyfold excess a complicated change in observed rotation took place, which has been discussed elsewhere (Schwab and Rund 1970).

The observed rotations were measured at the irradiation wavelength. Consequently the rates at each energy cannot be directly compared.

Table 3. Results of Irradiation of  $[\text{Rh}(\text{phen})_2\text{Cl}_2]^{+1}$ .

Irradiation wavelength, m $\mu$	Absorbance <sup>b</sup>	$10^3$ (change in rotation), degrees	Time interval, minutes
273	1.63	6.4	300
336	0.130	5.1	650
353	0.125	1.4	120
dark	0.180	0	2,880

a. Solvent, 0.01 M  $\text{NaClO}_4$ ; T = 30 $^\circ$ .

b. Absorbance is at irradiation wavelength; dark sample at 353 m $\mu$ .



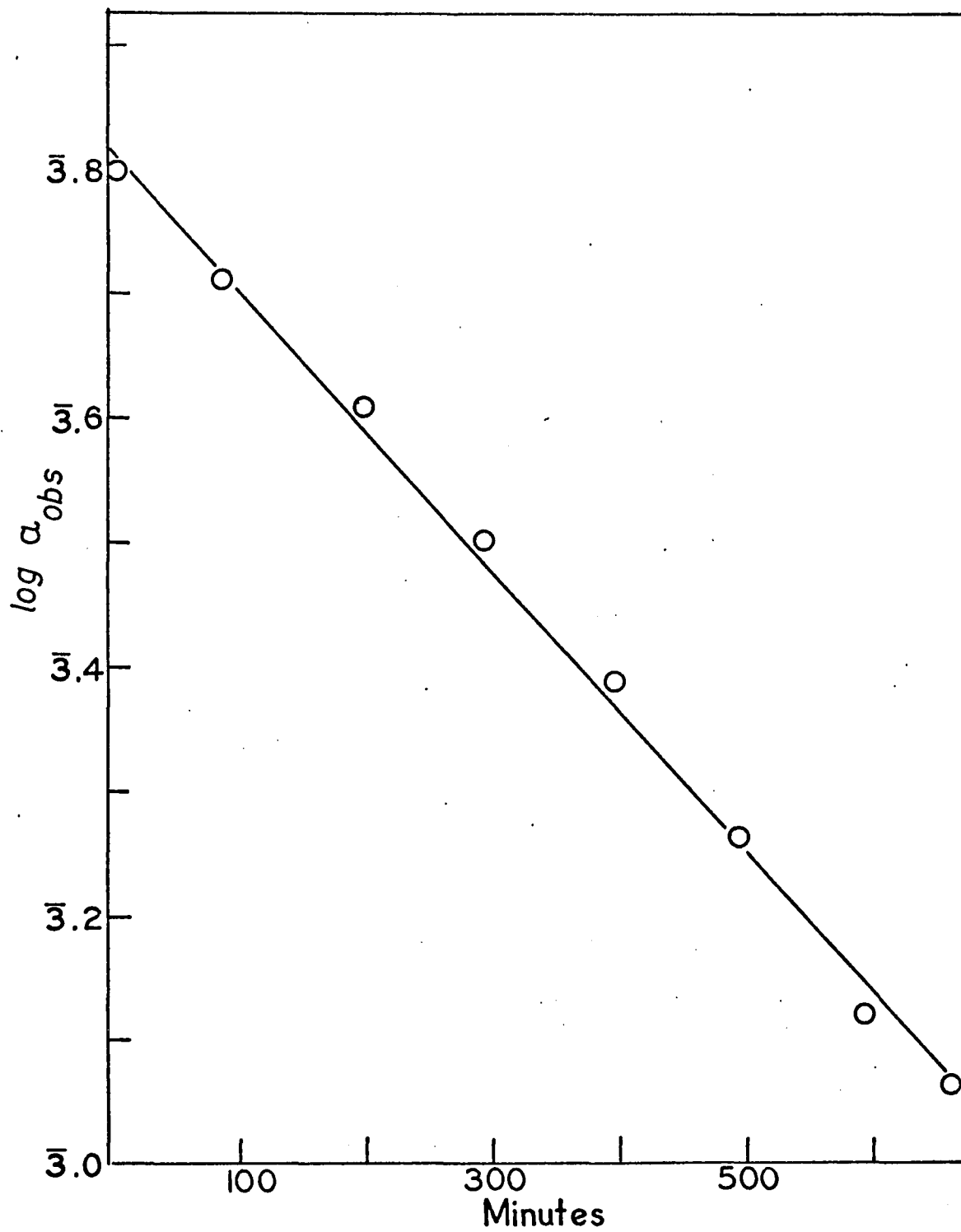


Figure 5. Sample plot. Irradiation of  $[\text{Rh}(\text{phen})_2\text{Cl}_2]^{+1}$  at 336 m $\mu$ .  
Second entry in Table 3.

## CHAPTER 4

### CONCLUSION

At 25°,  $\text{Co}(\text{acac})_3$  photoracemization occurs at 297, 322, and 595  $\mu$  at rates substantially greater than thermal racemization. The quantum yield is independent of wavelength. Photodecomposition is not a serious competitive reaction at 25°, but at 55° both decomposition and thermal racemization become inconveniently large.

The complex  $\text{Cr}(\text{acac})_3$  photoracemizes with moderate decomposition at 338  $\mu$ . No photoracemization was detected at 295 or 560  $\mu$ .

In the solid state  $\text{K}_3[\text{Cr}(\text{ox})_3]$  clearly undergoes thermal racemization. No clear increase in loss of optical rotation was seen when samples were irradiated. Large decreases were observed but they are due to an unidentified third process.

Rapid photoracemization occurs when  $\text{cis-}[\text{Rh}(\text{phen})_2\text{Cl}_2]^{+1}$  is irradiated in 0.01  $M$   $\text{NaClO}_4$  at 273, 336, or 353  $\mu$ . No photodecomposition or thermal racemization was detected. Moderate amounts of Rh(I) species do not catalyze racemization.

PART II - A KINETIC STUDY OF THE REACTION OF 1,10-PHENANTHROLINES  
AND 2,2'-DIPYRIDYLS WITH SQUARE-PLANAR METAL COMPOUNDS

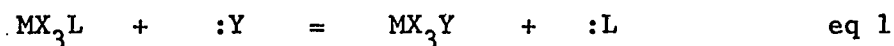
## CHAPTER 1

### INTRODUCTION

Until recently the only extensively studied substitution processes of square-planar complexes were those of platinum(II).

#### Normal Substitution

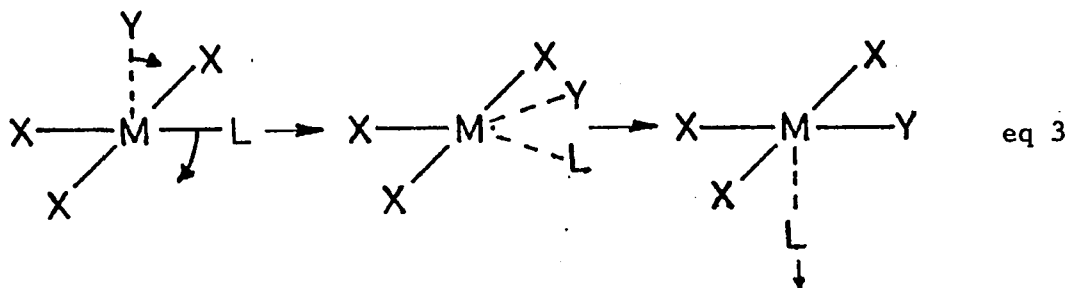
Nucleophilic attack with associative activation is consistent with the bulk of ligand substitutions studied for square-planar platinum. The typical substitution reaction (eq 1) is best explained by a bimolecular displacement mechanism (Basolo and Pearson 1967, chap. 5; Langford and Gray 1965, chap 2).



A two-term rate law is generally followed, e.g.:

$$\text{Rate} = k_1(\text{MX}_3\text{L}) + k_2(\text{MX}_3\text{L})(\text{Y}) \quad \text{eq 2}$$

which requires a parallel path mechanism. Considerable experimental evidence has led to a mechanism (eq 3) where the entering ligand, Y, attacks the complex,  $\text{MX}_3\text{L}$ , along an axis normal to the square-plane.



As Y enters, L begins to leave. At some point along the reaction coordinate the entering group, the leaving group, the ligand trans to them, and the metal ion form a trigonal plane. Y continues to approach and L continues to leave until Y is in the square-plane and the leaving group is in a labile axial position and is quickly lost.

This scheme accounts for the second-order term,  $k_2(\text{MX}_3\text{L})(\text{Y})$ , in the rate law. The first-order term,  $k_2(\text{MX}_3\text{L})$ , is attributed to a solvent molecule, S, participating in the above scheme as an entering group, forming  $\text{MX}_3\text{S}$ . The solvent is then very rapidly displaced by a molecule via the repetition of the same process. Solvolysis is the rate determining step for this path.

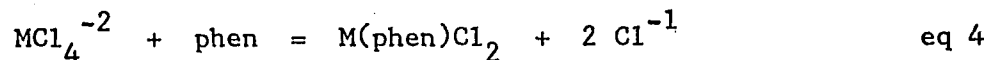
The constant  $k_1$  characterizes the replacement of L by solvent which is then quickly replaced by Y. Direct replacement of L by Y is controlled by  $k_2$ . Langford and Gray (1965, chap. 2) have collected evidence which indicates these two processes have associative activation and a trigonal-bipyramidal intermediate that is stabilized relative to the prior transition state. The few examples of other metals studied which form  $d^8$ , square-planar complexes also follow this model.

Since attack of the entering group is along an axis normal to the plane of the complex, the entering ligand must move from the general solution to a site in an outer-sphere complex. This in general will be a reversible, equilibrium process. If this site is near the z-axis, the ligand can move into the inner-sphere complex where bond-making may begin. It is important then that the ligand be in the proper position (along a nonligated axis). Any feature of the system which would favor

the occupancy of a special position may be expected to affect the reaction rate. Overcoming the statistical occurrence of the entering group at the axis might be helped by coulombic effects such as ion-ion or ion-dipole interactions between the complex and the entering group.

#### Second-Order Reactions

Some examples are known which deviate from this "normal" mechanism (e.g., Martin 1967, Palocsay and Rund 1969, Rund 1970a, Cawley and Rund 1970). In particular the work by Rund and co-workers has shown that for the reactions



(M is Pt(II) or Pd(II) and phen is 1,10-phenanthroline)

the rate is unusually slow. Not only is the second-order term slower but the replacement of solvent by the ligand is so retarded that it became the rate-determining step for the solvent path. The net rate is now second-order since each parallel path is second-order, leading to the new rate law:

$$\text{Rate} = k_o (MX_3L)(Y) \quad \text{eq 5}$$

The unusual slowness has been primarily attributed to the bulkiness and inflexibility of the entering group.

A second unusual property of this system is the insensitivity of rate to basicity of the entering ligand. This behavior has led to

the postulation of a dissociative interchange,  $I_d$ , mechanism for this reaction (Rund 1970a).

#### Mechanisms

As designated by Langford and Gray (1965, chap. 1) the dissociative interchange mechanism will have dissociative activation, with only weak (perhaps extremely weak) bonding to both the entering and leaving groups. The entering group effect on the rate will be small or non-detectable. The leaving group, solvent or ionic strength will affect the reaction energetics more.

The normal mechanism by which square-planar complexes react (eq 2) is designated Associative, A. There will be associative activation with substantial bonding to both the entering and leaving groups. The reaction energetics will be substantially affected by the nature of the entering group.

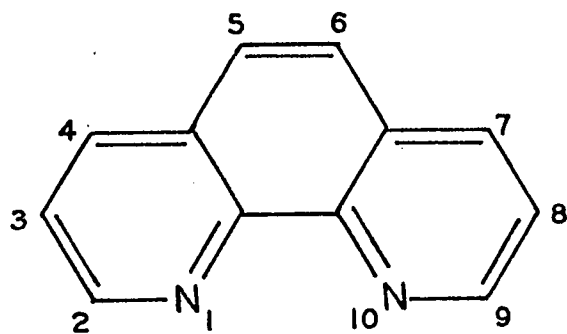
There is an intermediate mechanism in the Langford and Gray classification. Associative interchange,  $I_a$ , which involves an energetic contribution by the entering group which is important and detectable, but not dominant, in determining the energy of the transition state.

#### Purpose of This Investigation

Investigation of this reaction using dipyridyl may clarify the factors which account for the non-associative mechanism. Dipyridyl and phenanthroline have almost the same basicity ( $pK_a = 4.5$  and  $4.9$ , respectively) and polarizability (based on structure).

One important difference between the two ligands is their flexibility. Phenanthroline is rigidly fixed in a plane by the 5,6-bridge (see Figure 6). Absence of this bridge in dipyridyl allows rotation about the 2,2'-bond. Dipyridyl is known to be trans in benzene solution (Fielding and LeFevre 1951). Molecule models show that this flexibility allows dipyridyl to act as a monodentate ligand. Extreme crowding is indicated when only a single coordination site is occupied.





1,10-phenanthroline

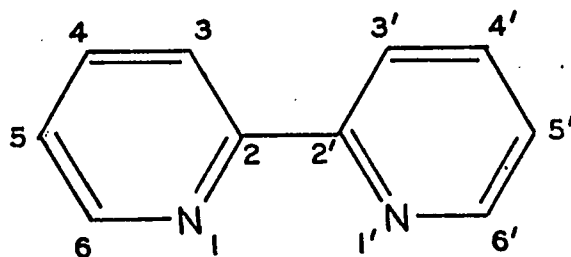
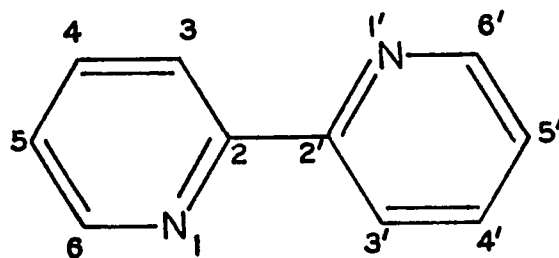
2,2'-dipyridyl, cis2,2'-dipyridyl, trans

Figure 6. Structure of phenanthroline and dipyridyl.

## CHAPTER 2

### EXPERIMENTAL

#### Chemicals

The complex  $K_2PtCl_4$  was synthesized by a literature method (Keller 1946, Kauffman and Teter 1963). Anal. Calcd for  $K_2PtCl_4$ : Cl, 34.16. Found: Cl, 34.13.

The complex  $K_2PdCl_4$  was prepared from metallic palladium (Rund 1970a). Anal. Calcd for  $K_2PdCl_4$ : Cl, 43.47. Found: Cl, 43.14.

The reaction product  $[Pt(dipy)Cl_2]$  was isolated from combined reaction mixtures as yellow needles. The ppt was collected, washed several times with hot water, and dried at  $100^\circ$ . Anal. Calcd for  $PtC_{10}H_8N_2Cl_2$ : C, 28.50; H, 1.90; Cl, 16.60. Found: C, 28.53; H, 2.09; Cl, 16.85.

The reaction product  $[Pd(dipy)Cl_2]$  was obtained in the same manner as the Pt analog above. Anal. Calcd for  $PdC_{10}H_8N_2Cl_2$ : C, 36.10; H, 2.40; Cl, 21.70. Found: C, 35.86; H, 2.60; Cl, 21.24.

#### Kinetics

##### Reaction Conditions

A 100-ml aqueous solution was made containing all reagents except the metal complex by dissolving dipyriddy1 (15.6 mg, 0.0001 moles), NaCl (sufficient to give desired chloride concentration), and  $NH_4BF_4$  (sufficient to bring the ionic strength to 0.274 M). After this solution had come to temperature in a constant temperature bath, the pH

was adjusted by the addition of either dilute  $\text{HNO}_3$  or  $\text{NaOH}$  solution until the desired pH was read on a pH meter (Leeds and Northrup #7410, calibrated against Leeds and Northrup buffer #103-1-0-1 at  $\text{pH} = 4.$ ).

The reaction was initiated by the addition of a weighed amount of complex to give a 1.0 mmolar concentration (31.0 mg of  $\text{K}_2\text{PdCl}_4$  or 39.4 mg of  $\text{K}_2\text{PtCl}_4$  in 95 ml of reaction mixture).

#### Determination of Reaction Progress

The reaction was monitored by measuring the disappearance of ligand. Five-ml aliquots of the reaction solution were withdrawn at intervals and the reaction was stopped by pipetting the sample into 15 ml of slightly acidic  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  solution (0.40 g/l) containing  $\text{NaCl}$  (12.0 g/l). A red color rapidly developed as ferrous ion complexed the free dipyridyl to form  $\text{Fe}(\text{dipy})_3^{+2}$ . The solutions were filtered after 1000 seconds to remove the insoluble reaction product; after 2400 seconds the absorbance was measured at 522  $\text{m}\mu$  on a Beckman Model DU spectrophotometer.

#### Determination of Observed Rate Constant

The complex and ligand were always present at equal concentrations;  $k_{\text{obsd}}$  was determined from a plot of time versus reciprocal of the free dipyridyl concentration.

## CHAPTER 3

### RESULTS

#### The Reaction of $K_2PdCl_4$ With Dipyridyl

Dipyridyl is consumed by a second-order process in solutions which contain  $K_2PdCl_4$ . Second-order plots are linear for a minimum of 75% reaction (see Figure 7). Complexes obeying the two-term rate law (eq 2) proceed principally through the first-order path. Pseudo first-order conditions (i.e., high ligand concentrations) are usually used to evaluate the normal system. Even when the ligand and complex are present at similar concentrations, second-order plots are not linear. First-order contribution to the rate was highly favored by the equimolar concentrations of complex and ligand used in these experiments. It was not detected.

The variation in observed rate constant,  $k_{obsd}$ , with chloride concentration is listed in Table 4. In the rate expression (eq 5) the observed rate constant as a function of chloride concentration is given by eq 6, where  $k_{H_2O}$  is the rate constant for ligand attack of the aquated species,  $MCl_3(H_2O)^{-1}$ , and  $k_{Cl}$  is the rate constant for ligand

$$k_{obsd} = \frac{k_{H_2O} K_{eq} + k_{Cl} [Cl^{-1}]}{K_{eq} + [Cl^{-1}]} \quad \text{eq 6}$$

attack on the tetrachloro complex. The equilibrium constant,  $K_{eq}$ , is for aquation of the tetrachloro complex. Using  $k_{H_2O}$ ,  $k_{Cl}$ , and  $K_{eq}$  as

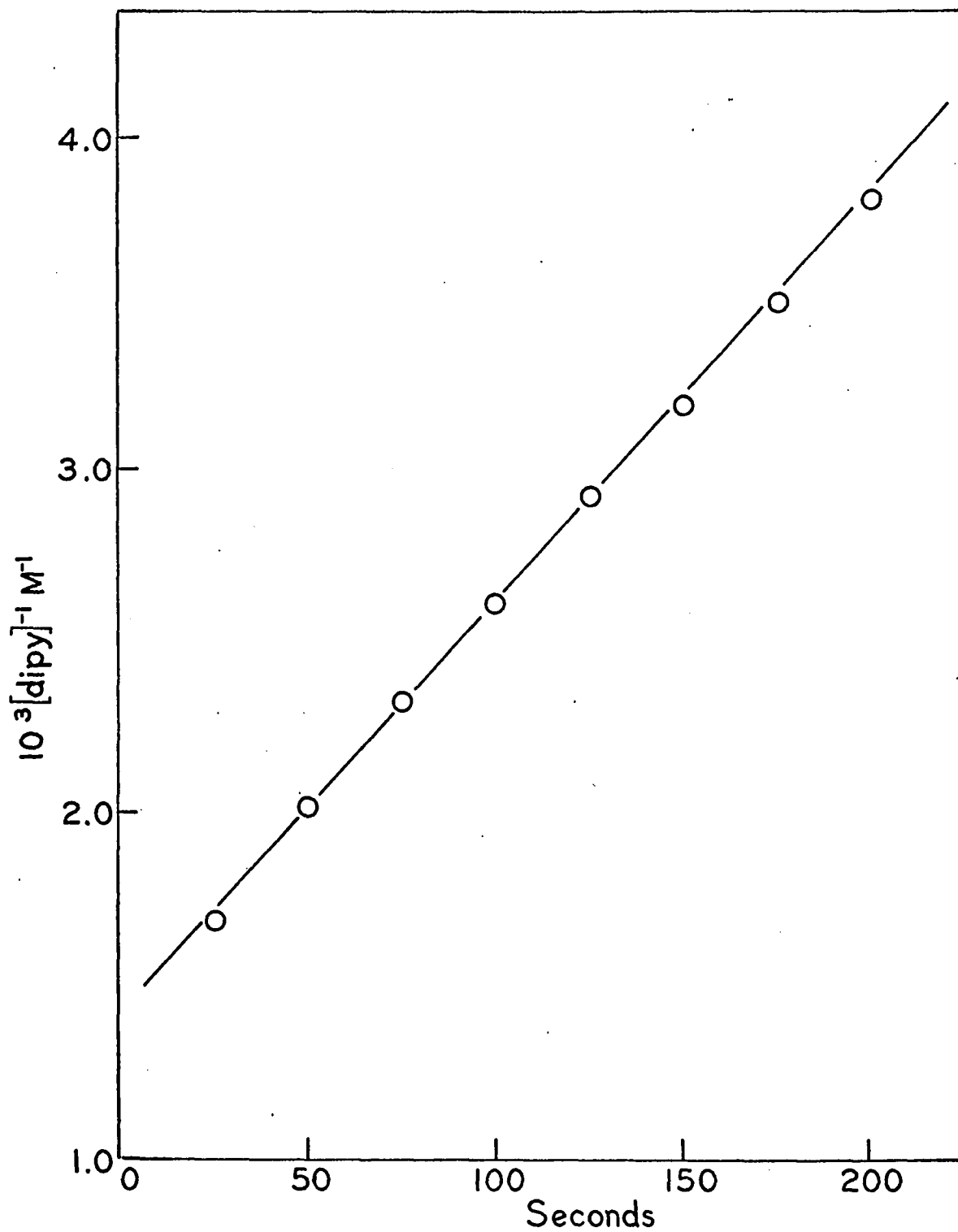


Figure 7. Sample plot. Second-order disappearance of dipy.

Conditions as in entry 4 in Table 4. Half-life is 50 sec.

Table 4. Reaction between  $K_2PdCl_4$  and dipy. The second-order rate constant as a function of  $[Cl^{-1}]$ .

$[Cl^{-1}]$ , <u>M</u>	$k_{obsd}$ , $\underline{M}^{-1}sec^{-1}$ <sup>a</sup>	$k_{calcd}$ , $\underline{M}^{-1}sec^{-1}$ <sup>b</sup>
0.275	$5.1 \pm 0.2$	4.9
0.208	$6.2 \pm 0.3$	6.0
0.138	$7.6 \pm 0.4$	7.9
0.0694	$13.2 \pm 1.5$	11.4
0.0352	$17.8 \pm 2.7$	18.2
0.0181	$20.6 \pm 3.9$	24.1
0.0101	$28.5 \pm 5.0$	28.4
0.00579	$32.4 \pm 5.1$	31.5

a.  $[PdCl_4^{-2}] = [dipy] = 1 \times 10^{-3}$  M, pH = 3.3,  $\mu = 0.275$  M,  $T = 50^\circ$ .

b. Calculated from eq 6 for  $k_{Cl} = 1.2 \underline{M}^{-1}sec^{-1}$ ,  $k_{H_2O} = 37 \underline{M}^{-1}sec^{-1}$  and  $K_{eq} = 0.0032 \underline{M}$ .

parameters, values for  $k_{\text{obsd}}$  (now called  $k_{\text{calcd}}$ ) were calculated at each chloride concentration. The  $k_{\text{calcd}}$  values obtained are listed in Table 4 for the solution  $k_{\text{H}_2\text{O}} = 37 \text{ M}^{-1}\text{sec}^{-1}$ ,  $k_{\text{Cl}} = 1.2 \text{ M}^{-1}\text{sec}^{-1}$  and  $K_{\text{eq}} = 0.032 \text{ M}$ . No significant improvement in  $k_{\text{calcd}}$  is obtained by adjusting the parameters. The agreement between observed and calculated constants validates the parallel second-order mechanism.

The ionic strength,  $\mu$ , also affects the rate as shown in Table 5. The inverse effect of ionic strength on the rate constant supports, but does not establish, reaction between ions of opposite charge. It has been pointed out that the Brønsted-Bjerrum-Christiansen equation does not apply to the reaction conditions used (Frost and Pearson 1962, Palocsay and Rund 1969, Rund 1970a). Both the high ionic strength and the difference in activated complex for these reactions do not resemble the conceptual model.

The rate of reaction is also a function of pH (Table 6 and Figure 8). There are three separate ways which the pH may alter the rate constants:

1. At high hydrogen ion concentration the reaction between ferrous ion and free dipyridyl is retarded. The value of  $k_{\text{obsd}}$  appears to change because the reaction is not stopped quickly enough to prevent further substitution of the substrate. This dependence is apparent at about  $\text{pH} = 2.9$  or less.

2. The  $\text{pK}_a$  of dipyridyl is 4.5 at  $25^\circ$  (McBryde 1965). The equilibrium between dipyridyl and dipyridylium ion will be strongly effected as the pH is changed near the  $\text{pK}_a$ . If one form of the ligand

Table 5. Reaction between  $K_2PdCl_4$  and dipy. The second-order rate constant as a function of ionic strength.

$\mu$ , <u>M</u>	$k_{obsd}$ , $\underline{M}^{-1} \text{ sec}^{-1a}$
0.0387	$27.2 \pm 0.9$
0.100	$23.4 \pm 1.3$
0.150	$18.7 \pm 1.6$
0.275	$17.8 \pm 2.7$ (18.2 calcd)

a.  $[PdCl_4^{-2}] = [dipy] = 1 \times 10^{-3} \underline{M}$ , pH=3.3, T=5°,  $[Cl^{-1}] = 0.0352 \underline{M}$ .

Table 6. Reaction between  $K_2PdCl_4$  and dipy. The second-order rate constant as a function of pH.

pH	$k_{obsd}$ , $\underline{M}^{-1} \text{ sec}^{-1a}$
2.0	-b
2.9	$7.2 \pm 1.4$
3.1	$6.0 \pm 0.3$
3.3	$6.2 \pm 0.3$
4.2	$5.7 \pm 0.6$
4.7	$6.1 \pm 0.6$
5.0	$6.4 \pm 0.2$
6.0	$11.5 \pm 0.4$
7.0	$23.5 \pm 9$

a.  $[PdCl_4^{-2}] = [dipy] = 1 \times 10^{-3} \underline{M}$ ,  $\mu = 0.275 \underline{M}$ , T=5°,  $[Cl^{-1}] = 0.208 \underline{M}$ .

b. Color did not develop fully after 2400 seconds.



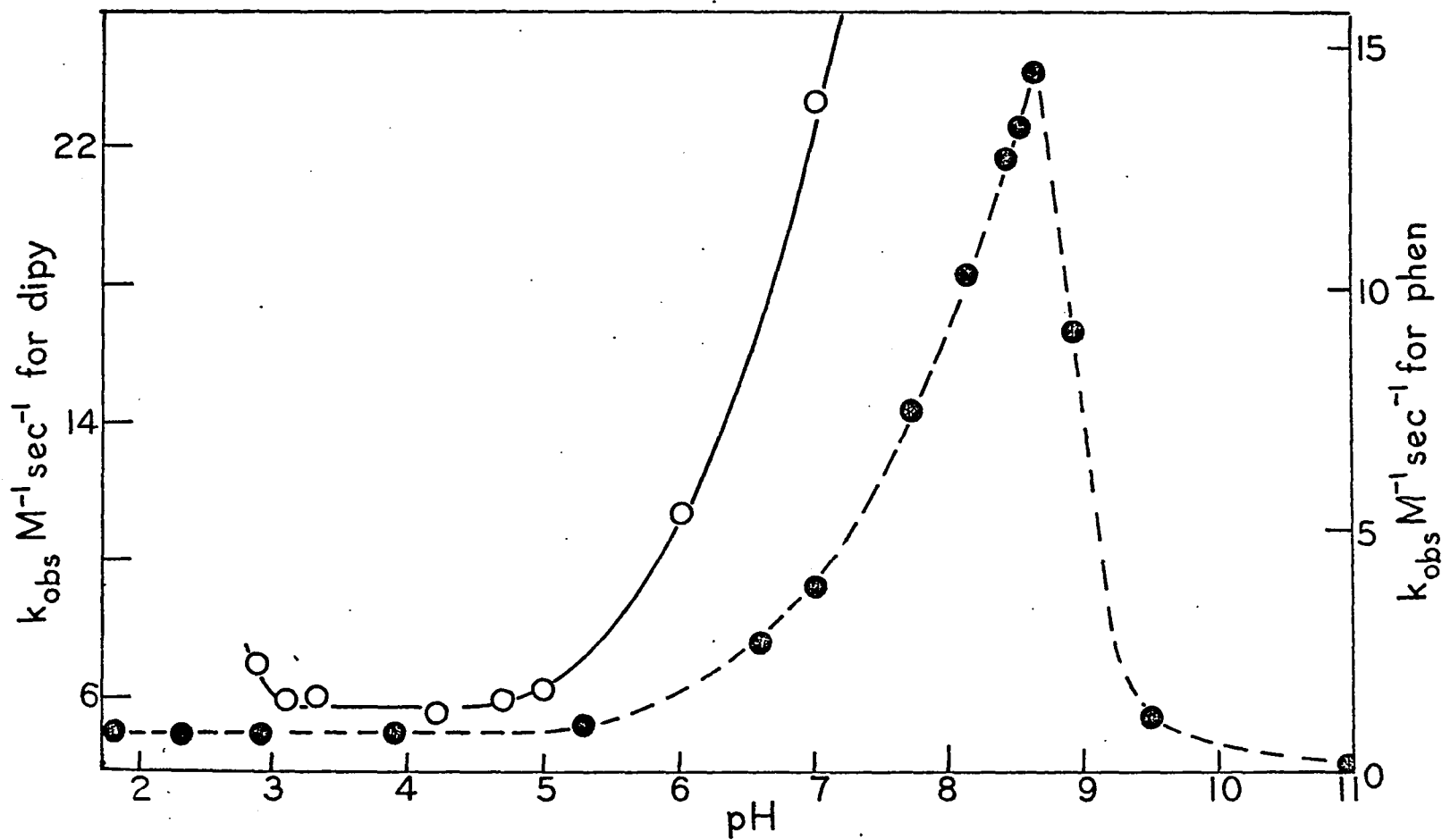


Figure 8. Second-order rate constant as a function of pH for the reaction of  $K_2PdCl_4$  + ligand.  $\circ$  dipy, conditions as in Table 6;  $\bullet$  phen, data taken from Rund (1970a).

is a better nucleophile than the other, a rate dependence should be observed. As the pH is changed from 3.1 to 5.0 the ratio of  $\text{dipyH}^+$  to dipy changes from 16 to 0.2, or 80-fold. The rate constant is invariable within experimental error over this range.

3. Above  $\text{pH} = 5.0$  the rate increases sharply due to the deprotonation of the aquo complex,  $\text{MCl}_3(\text{H}_2\text{O})^{-1}$ , to form a hydroxo complex,  $\text{MCl}_3(\text{OH})^{-2}$ , which reacts with the ligand much more rapidly (Cawley and Rund 1970, Rund 1970a). The similarity for phen and dipy is shown in Figure 8. The sharp decrease in rate constant above  $\text{pH} = 8.6$  for phen is attributed to precipitation of palladium(II) oxide (Rund 1970a) and was not reinvestigated.

#### The Reaction of $\text{K}_2\text{PtCl}_4$ With Dipyridyl

A parallel second-order mechanism accounts for the substitution of  $\text{K}_2\text{PtCl}_4$  by dipyridyl. The disappearance of dipyridyl fits second-order plots of  $[\text{dipy}]^{-1}$  versus time, e.g., Figure 9. No curvature due to a first-order contribution was observed.

Table 7 lists  $k_{\text{obsd}}$  as a function of chloride concentration and  $k_{\text{calcd}}$  obtained from eq 6 when  $k_{\text{Cl}} = 0.27 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{H}_2\text{O}} = 2.9 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  and  $K_{\text{eq}} = 1.5 \times 10^{-2} \text{ M}$ . No better fit is obtained by adjusting the values of these constants.

The rate constant shows a dependence on ionic strength (Table 8). Again the rate decreased when the ionic strength increased. The "slow" reaction for  $\mu = 0.0387 \text{ M}$  was verified. This particular solution was the only one which did not contain  $\text{NH}_4\text{BF}_4$ ; the ionic strength is due solely to complex, ligand, and NaCl.

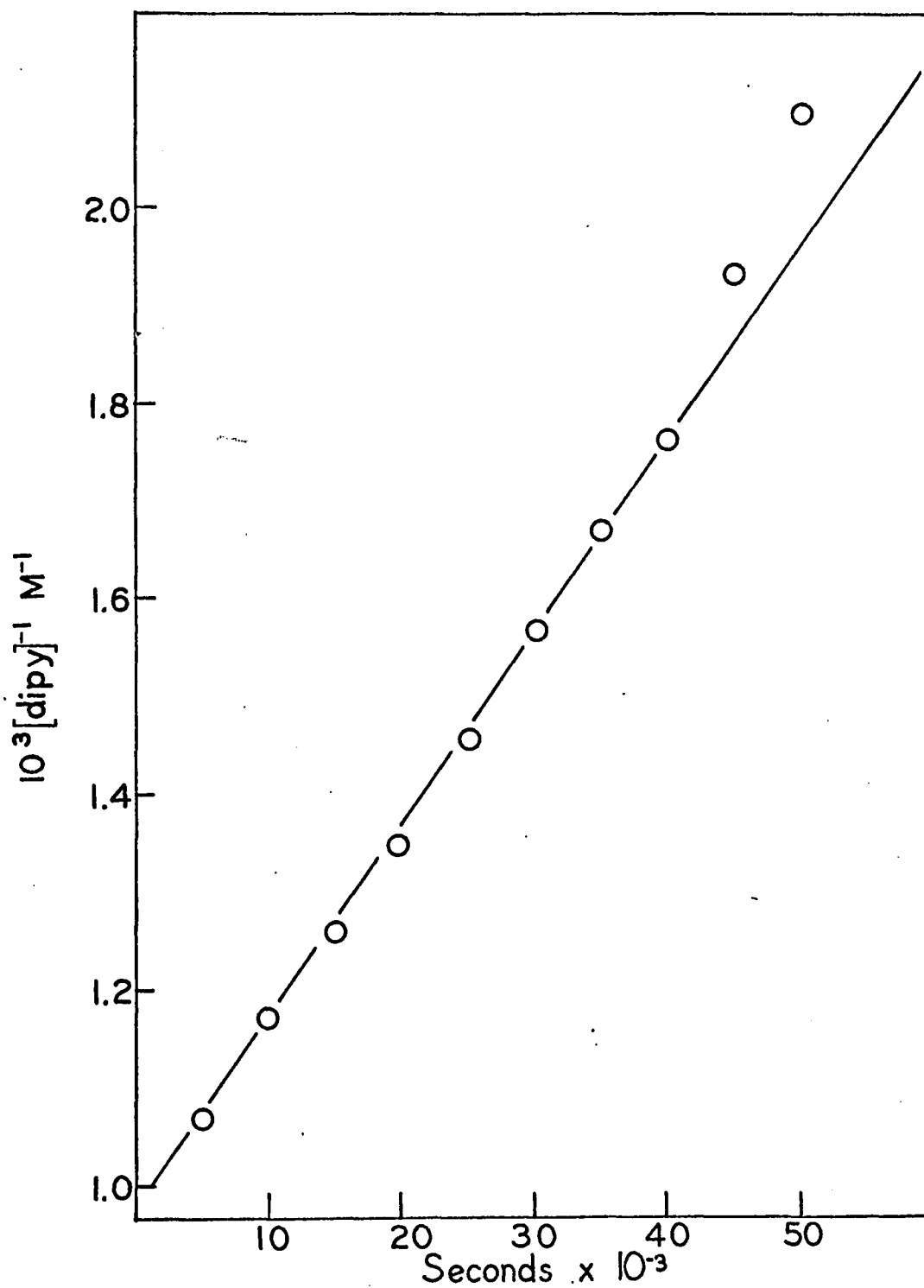


Figure 9. Sample plot. Second-order disappearance of dipy.

Conditions as in entry 7 in Table 7. Half-life is 45,000 sec.

Table 7. Reaction between  $K_2PtCl_4$  and dipy. The second-order rate constant as a function of  $[Cl^{-1}]$ .

$[Cl^{-1}]$ , <u>M</u>	$k_{obsd} \times 10^3$ , <u>M</u> <sup>-1</sup> <u>sec</u> <sup>-1</sup> <sup>a</sup>	$k_{calcd} \times 10^3$ , <u>M</u> <sup>-1</sup> <u>sec</u> <sup>-1</sup> <sup>b</sup>
0.274	4.5 ± 0.6	4.1
0.207	4.7 ± 1.5	4.5
0.136	5.1 ± 0.7	5.3
0.0683	7.1 ± 0.7	7.5
0.0342	11.9 ± 1.9	10.7
0.0171	14.9 ± 0.8	14.9
0.00909	19.8 ± 0.5	19.0
0.00480	22.6 ± 0.5	22.6

a.  $[PtCl_4^{-2}] = [dipy] = 1 \times 10^{-3}$  M, pH = 2.9,  $\mu = 0.275$  M, T = 55°.

b. Calculated using eq 6 when  $k_{Cl} = 0.27 \times 10^{-2}$  M<sup>-1</sup>sec<sup>-1</sup>,  $k_{H_2O} = 2.9 \times 10^{-2}$  M<sup>-1</sup>sec<sup>-1</sup>, and  $K_{eq} = 1.5 \times 10^{-2}$  M.

Table 8. Reaction between  $K_2PtCl_4$  and dipy. The second-order rate constant as a function of ionic strength.

$\mu$ , <u>M</u>	$k_{\text{obsd}} \times 10^3$ , $\underline{M}^{-1}\text{sec}^{-1\text{a}}$
0.0387	$14.4 \pm 1.5$
0.100	$19.0 \pm 0.4$
0.150	$14.3 \pm 0.5$
0.274	$11.9 \pm 1.9$ (10.7 calcd)

a.  $[PtCl_4^{-2}] = [dipy] = 1 \times 10^{-3} \underline{M}$ , pH = 2.9, T = 55°,  $[Cl^{-1}] = 0.0342 \underline{M}$ .

Table 9. Reaction between  $K_2PtCl_4$  and dipy. The second-order rate constant as a function of pH.

pH	$k_{\text{obsd}} \times 10^3$ , $\underline{M}^{-1}\text{sec}^{-1\text{a}}$
2.9	$4.7 \pm 1.5$
3.3	$4.7 \pm 0.9$
3.9	$5.1 \pm 0.2$
4.3	$4.6 \pm 0.2$
4.7	$2.2 \pm 0.6$
5.0	$2.2 \pm 0.6$
6.0	$2.3 \pm 0.1$
6.5	$1.9 \pm 0.1$

a.  $[PtCl_4^{-2}] = [dipy] = 1 \times 10^{-3} \underline{M}$ ,  $\mu = 0.275 \underline{M}$ , T = 55°,  $[Cl^{-1}] = 0.207 \underline{M}$ .

The  $K_2PtCl_4$  reaction exhibits a very different pH dependence from  $K_2PdCl_4$ . Table 9 contains the rate constants observed at various pH values. These results are plotted in Figure 10; also presented is the pH dependence of  $K_2PtCl_4$  when phen is the ligand. The reaction with phen is the same as when  $K_2PdCl_4$  reacted with either phen or dipy, i.e., no entering group effect, but definite acceleration as hydroxo complex forms.

The reaction involving the platinum complex and dipy shows a small but definite rate change upon protonation of the ligand. The observed rate constant is about doubled when dipyridylium ion is the entering ligand compared to attack by dipyridyl itself.

Conspicuously absent is acceleration of the reaction at pH's of 6.0 and above. There is no detectable leaving group effect when hydroxo complex forms, as was the case for  $K_2PtCl_4$  and phen,  $K_2PdCl_4$  and phen, or  $K_2PdCl_4$  and dipy reactions.

### Mechanisms

#### Intimate Mechanism

The results for  $K_2PdCl_4$  + dipy are the same as for phen and both  $K_2PdCl_4$  or  $K_2PtCl_4$ . No entering group effect is observed when the ligand is changed from the base form to the conjugate acid form. Leaving group effect is evident. The rate constants  $k_{H_2O}$  and  $k_{Cl}$  are different by a factor of about 30, so water is a considerably better leaving group than chloride. Better than either of these is hydroxide ion. At pH = 7.0 the observed rate is rising rapidly; so rapid is the rate that the reaction becomes difficult to follow by the method used here. An

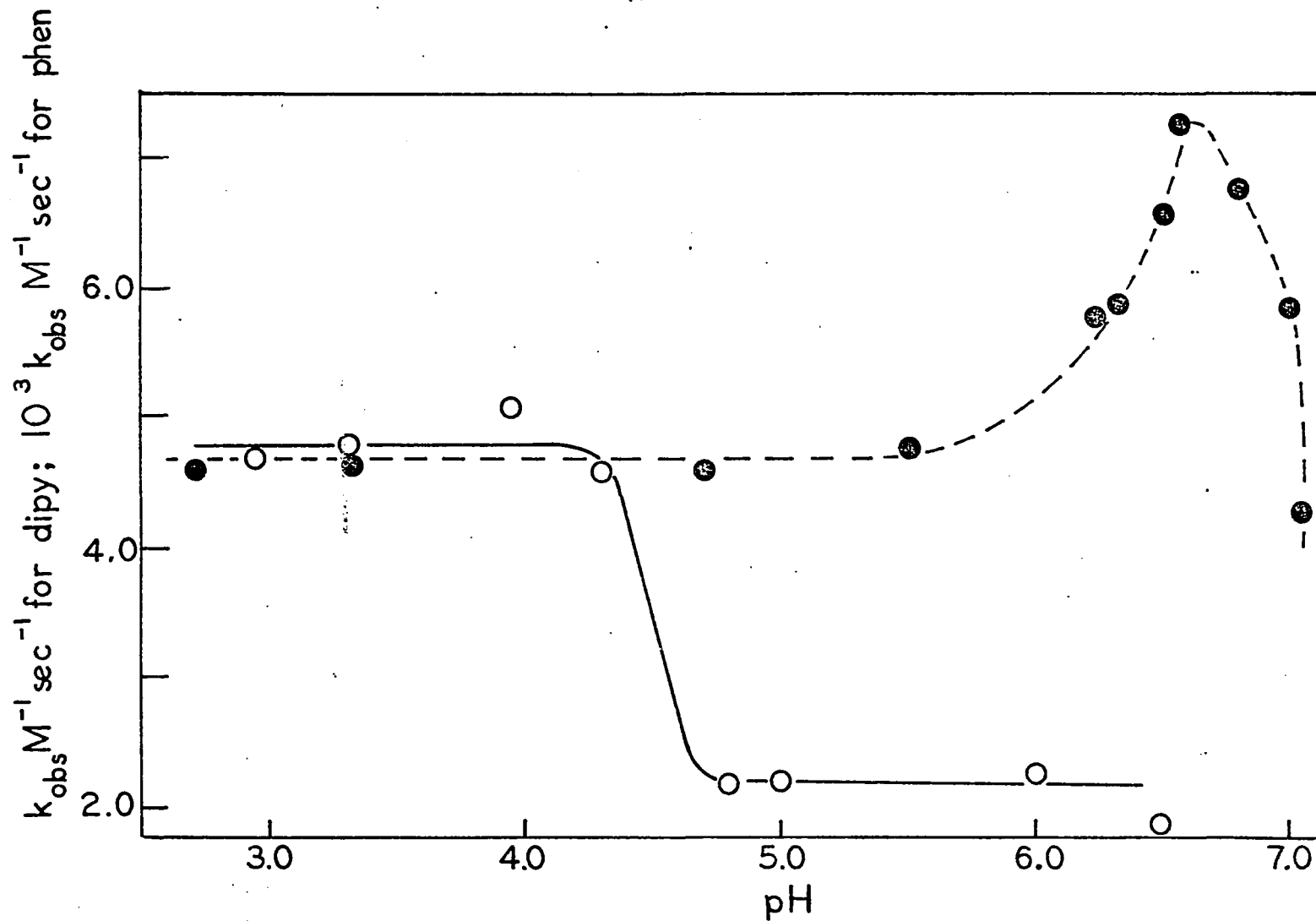


Figure 10. Second-order rate constant as a function of pH for the reaction of  $\text{K}_2\text{PtCl}_4$  + ligand.

○ dipy, conditions as in Table 9; ● phen, data taken from Cawley and Rund (1970).

evaluation of how much faster the reaction with hydroxide complex is cannot be determined, nor easily estimated. A conservative lower limit of 50 times faster for this reaction when phen is the ligand reactant has been established (Rund 1970a). Inspection of Figure 8 shows the dipy rate is rising sooner and more rapidly than the rate for phen at the same hydroxo complex concentration, i.e., pH. The intimate mechanism of these reactions is the same,  $I_d$ .

The intimate mechanism for the reaction between  $K_2PtCl_4$  and dipy must be significantly different from that proposed for the previous three systems. There are two distinct differences between the two situations. First, here we find a small but real entering group effect on the overall rate constant. When the ligand is protonated, it reacts with the complex faster. This is illustrated by the increase in rate constant below  $pH = 4.5$  in Figure 10 and Table 9. The protonated ligand assists attainment of the transition state. This type of assistance is called associative activation,  $a$ , of the reaction. Secondly, no detectable assistance was found for hydroxide as a leaving group. However, water is a much better leaving group than chloride and  $k_{H_2O}$  is about 10 times larger than  $k_{Cl}$ . Considering both the entering group and leaving group effects, the intimate mechanism is best described as  $I_a$ . An alternative is the A mechanism. However the lack of dominant entering group activation makes the A designation a less satisfying choice.

#### Stoichiometric Mechanism

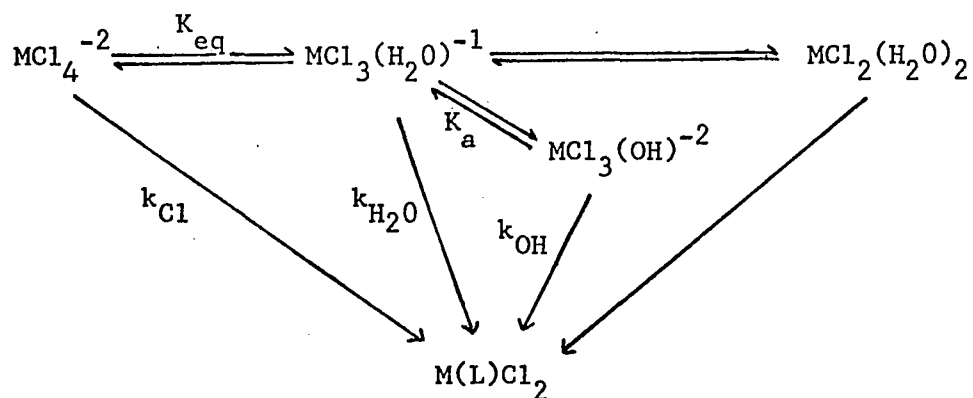
The stoichiometric mechanism is not so easily determined in full. It seems clear the complex  $MCl_4^{-1}$  is attacked by both (a) ligand, in a



slow, direct, bimolecular step which produces the observed reaction product,  $M(\text{dipy})\text{Cl}_2$ , and (b) water, in a faster, reversible step which leads to the equilibrium between the tetrachloro and trichloroquo species. Several fates are possible for the aquo complex:

1. Displacement of water by chloride to give the starting complex ion again.
2. Reversible ionization of the weak acid ligand, water, to give a trichlorohydroxo ion.
3. Displacement of a second chloride by water to give a dichlorodiaquo complex.

There are at least these four species which may undergo substitution by a ligand molecule. This reaction scheme is depicted below with some of the appropriate constants indicated.



The attack of ligand on both  $\text{MCl}_4^{-2}$  and  $\text{MCl}_3(\text{H}_2\text{O})^{-1}$  are well established for "normal" substitution reactions of square-planar complexes. This mechanism accounts for the results of the reaction between  $\text{K}_2\text{PtCl}_4$  and dipy; but for palladium complex and dipy, an additional path for substitution is necessary. It must be pH dependent and provide for

acceleration of the rate. Two choices are available. The ionization of aquo complex to form hydroxo species is certainly pH controlled. If hydroxide is a better leaving group than water, the rate will increase as observed. Hydroxide is generally considered to be a very poor leaving group (Langford and Gray 1965, p. 34; Basolo and Pearson 1967, p. 384). However no direct kinetic evidence has been published to support this idea. A strong case has been made for its relative lability when phen reacts with tetrachloroplatinum(II) or tetrachloropalladium(II) complexes (Cawley and Rund 1970, Rund 1970a).

An alternative intermediate species is possible, namely, the diaquo complex. The second aquation is catalyzed by hydroxide for  $\text{PtCl}_4^{-2}$  (Grantham, Elleman, and Martin 1955). Palladium complexes are expected to behave in the same manner. This would explain the pH dependence. On the other hand, the diaquo species is neutral as opposed to the negative aquo and hydroxo intermediates. The reaction of phen with neutral complexes of platinum is much slower than with anionic complexes. Neutral complexes of palladium did not react at all until an induction period passed; then a nonsecond-order reaction commenced (Rund 1970a). This kind of behavior was not observed here.

Having a water molecule as the leaving group for attachment of the second nitrogen atom of the bidentate ligand cannot increase the rate since the first attachment is the rate determining step. The diaquo complex does have a statistical advantage. It has two easily displaced leaving groups rather than just the one as in a monoquo complex.

Although diaquation is hydroxide catalyzed the rate of formation is much slower than monoquation (Grantham, Elleman, and Martin 1955). This would lead to an induction period at high pH before more rapid substitution could occur. No change in the form of the kinetic plots was observed as the pH was raised.

#### Ligand Effects

Dipyridyl reacts more rapidly than does phenanthroline with tetrachloro complexes of Pd(II) and Pt(II). Constants for the reaction are listed in Table 10. Usually polarizability rather than basicity has the more important role in determining the nucleophilic reactivity toward square-planar Pt(II) complexes (Edwards and Pearson 1962, Pearson 1963). What is more important, however, is the ability of the attacking ligand to form nonchelating intermediate complexes.

This observation can be related to the steric requirements of the transition state. The bulkiness of these bidentate ligands makes rapid reorientation of the ligand within the transition state complex difficult. Even in reactions involving polydentate entering groups, the chelate ring closes very rapidly in almost all cases (Holyer et al. 1965, Haake and Cronin 1963). The driving force for this is undoubtedly the chelate effect. These ideas can be combined into the single energetic requirement that the ligand must be specially positioned before activation can occur. The bulkiness of the ligand makes this difficult to do, but the extra driving force of the chelate effect makes it highly advantageous to do so.

Table 10. Second-order rate constants for various reactants.

Complex ligand	$K_2PdCl_4$		$K_2PtCl_4$	
	dipy .	phen <sup>a</sup>	dipy	phen <sup>b</sup>
$k_{Cl}, \underline{M}^{-1}sec^{-1}$	1.2	0.34	$0.27 \times 10^{-2}$	$0.27 \times 10^{-2}$
$k_{H_2O}, \underline{M}^{-1}sec^{-1}$	37	6.7	$2.9 \times 10^{-2}$	$1.2 \times 10^{-2}$
$K_{eq}, \underline{M}$	0.032	0.0094	$1.5 \times 10^{-2}$	$2.5 \times 10^{-2}$
$k_{OH^-}, \underline{M}^{-1}sec^{-1}$	-c	-c	-c	$21 \times 10^{-2}$
T, °	5	5	55	55
pH	3.3	3.3	2.9	2.0
$\mu, \underline{M}$	0.275	0.279	0.275	0.103

a. Rund, 1970b.

b. Palocsay and Rund, 1969.

c. Could not be evaluated, see text.

It is then understandable why these reactions are (1) unusually slow, (2) parallel second-order, and (3) nonassociatively activated. The complex requires a kind of "geometrical activation" and no part of the ligand begins bond making until the remainder of the ligand is oriented properly to quickly complete the substitution. Protonation of the ligand would certainly facilitate ion pair formation but will have no effect on the ability of the ligand to orient itself favorably. This accounts for the fact that no rate increase is observed at low pH, but orders of magnitude increases are observed for the increasingly flexible ligands, phen<dipy<en (Rund 1970a).

The system,  $K_2PtCl_4 + \text{dipy}$ , is sensitive to a small extent to protonation of the entering group. Pt(II) is less able to form five-coordinate species than Pd(II) (Langford and Gray 1965, p. 49), and therefore is more susceptible to energetic assistance by the entering group. Such assistance can be gained by coulombic interaction as the transition state is approached.

## CHAPTER 4

### CONCLUSIONS

When  $K_2PdCl_4$  reacts with dipy, it does so in the same manner as with phen, only at a more rapid rate. The reaction is still unusually slow, second-order, and insensitive to protonation of the ligand. Leaving groups accelerate the rate in the ratio: Cl(1),  $H_2O(30)$ ,  $OH^-(\gg 50)$ . The reaction has been interpreted as an  $I_d$  intimate mechanism. For reaction at  $5^\circ$  the reaction constants were determined to be  $k_{Cl} = 1.2 \underline{M}^{-1} \text{sec}^{-1}$ ,  $k_{H_2O} = 37 \underline{M}^{-1} \text{sec}^{-1}$ , and  $K_{eq} = 0.032 \underline{M}$ .

The complex  $K_2PtCl_4$  reacts with dipy in a way similar to  $K_2PdCl_4$ . The reaction is slower than with the Pd(II) complex but faster than when the ligand is phen. The reaction constants determined at  $55^\circ$  are:  $k_{Cl} = 0.27 \times 10^{-2} \underline{M}^{-1} \text{sec}^{-1}$ ,  $k_{H_2O} = 2.9 \times 10^{-2} \underline{M}^{-1} \text{sec}^{-1}$ , and  $K_{eq} = 1.5 \times 10^{-2} \underline{M}$ . An unusual characteristic of this particular set of reactants is the twofold rate acceleration by hydrogen ion. This appears to be due to protonation of the ligand, but is not currently understood. The entering group effect was not large compared to the leaving group effect: Cl(1),  $H_2O(10)$ . No rate acceleration was found when hydroxide was a leaving group. The reaction is interpreted as having an  $I_a$  mechanism.

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