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EXCHANGE IN METAL NITROSYLS.
PART II - A KINETIC STUDY OF THE REACTION
OF VARIOUS ORTHO-PHENANTHROLINES
WITH POTASSIUM TETRACHLOROPLATINATE
II.

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PART II - A KINETIC STUDY OF THE REACTION OF VARIOUS ORTHO-
PHENANTHROLINES WITH POTASSIUM TETRACHLOROPLATINATE II

by

Frank Alexander Palocsay

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Frank Alexander Palocsay

entitled Part I - A kinetic Study of Nitrosyl Exchange in Metal
Nitrosyls Part II - A Kinetic Study of the Reaction of
Various Ortho-Phenanthrolines with Potassium Tetrachloroplatinate II

be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

John V. Pineda
Dissertation Director

5 November 1968
Date

After inspection of the final copy of the dissertation, the
following members of the Final Examination Committee concur in
its approval and recommend its acceptance:*

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Nov 5, 1968
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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	vii
LIST OF TABLES	ix
ABSTRACT	xi
PART I - A KINETIC STUDY OF NITROSYL EXCHANGE IN METAL NITROSYLS	1
CHAPTER	
1 INTRODUCTION	2
CO Exchange in Ni(CO) ₄ and Related Compounds	3
Co(CO) ₃ NO	4
Metal Carbonyls and Phosphorus Trifluoride	4
2 PURPOSE	6
3 EXPERIMENTAL	7
Synthesis of Cobalt Tricarbonyl Nitrosyl	7
Nickel Cyclopentadienyl Nitrosyl	8
Apparatus for NO Substitution	8
Apparatus for NO Exchange	9
Substitution Reaction	12
N ¹⁵ O Exchange Reaction	13
Determination of the Rate Constants in the Exchange Reaction	13
Determination of the Rate Constants in the Substitution Reaction of NO on Co ₂ (CO) ₈	14
4 RESULTS	15
The Substitution Reaction of Co ₂ (CO) ₈ by NO	15
The Exchange Reaction of Co(CO) ₃ NO with ¹⁵ NO	19
The Exchange Reaction of Fe(CO) ₂ (NO) ₂ with ¹⁵ NO	23
The Exchange Reaction of (C ₅ H ₅)Ni(NO) with ¹⁵ NO	23
5 CONCLUSIONS	24

TABLE OF CONTENTS--Continued

	Page
PART II - A KINETIC STUDY OF THE REACTION OF VARIOUS ORTHO-PHENANTHROLINES WITH POTASSIUM TETRACHLOROPLATINATE II .	31
CHAPTER	
1 INTRODUCTION	32
Substitution Reactions of Transition Metal Complexes with 1,10-Phenanthroline	34
The Substitution Reactions of Some Transition Metals at a +2 Oxidation State with 1,10-Phenanthroline	35
The Kinetics of Complex Formation of Nickel(II) . .	36
2 PURPOSE	41
3 EXPERIMENTAL	42
K ₂ PtCl ₄	42
Pt(phen)Cl ₂	42
Rates of Substitution Reactions	43
Equilibrium Constants and Rates of Aquation of K ₂ PtCl ₄	44
The Rate of Decomposition of K ₂ PtCl ₄ in 50% Ethanol	45
4 RESULTS	46
The Substitution Reaction of K ₂ PtCl ₄ by 1,10-Phenanthroline in Water	46
The Rate Dependence on Changing Chloride Ion Concentration	48
The Aquation Reaction of PtCl ₄ ⁼	48
The Effect of Changing Ionic Strength	48
The Effect of Changing pH	51
The Effect of Other Ligands on the Rate of the Substitution Reaction	52
The Reaction of PtCl ₄ ⁼ with 1,10-Phenanthroline in Mixed Solvents	52
The Solvolysis of K ₂ PtCl ₄ in 50% Ethanol	59
Dependence of the Rate on Chloride Ion Concentration	60

TABLE OF CONTENTS--Continued

	Page
The reaction Between K_2PtCl_4 and 1,10-Phenanthroline in the Presence of Possible Catalysts	60
Hydride Ion	61
Ethylene	61
Platinum Metal	63
Platinum(O)	63
Mixed Solvents Other Than Ethanol-Water	64
5 CONCLUSIONS	68
The Aqueous Reaction	68
The Reaction of K_2PtCl_4 with 1,10-Phenanthroline in Mixed Solvents	74
REFERENCES	78

LIST OF ILLUSTRATIONS

Figure		Page
PART I		
1.	The Reaction Vessel for the Nitric Oxide Substitution Reaction of $\text{Co}_2(\text{CO})_8$	10
2.	Glass Bulb for the Nitric Oxide Exchange Experiments	10
3.	Chemical Storage and Sampling System	11
4.	The Rate of Formation of $\text{Co}(\text{CO})_3\text{NO}$ in Hexane Versus Time at 0°C	16
5.	Possible Mechanisms for CO Exchange in $\text{Co}_2(\text{CO})_8$	18
6.	Possible Mechanisms for the NO Substitution of $\text{Co}_2(\text{CO})_8$	18
7.	The Rate of Nitric Oxide Exchange of $\text{Co}(\text{CO})_3\text{NO}$ Versus Time at 35°C	20
8.	The First-order Rate of Nitric Oxide Exchange of $\text{Co}(\text{CO})_3\text{NO}$ Versus the Concentration of ^{15}NO	22
9.	Possible Structures of $\text{Co}(\text{CO})_3(\text{NO})_2$	27
PART II		
10.	The Structure of 1,10-Phenanthroline	33
11.	The Suggested Resonance Forms of 1,10-Phenanthroline- metal Complexes	33
12.	The Rate of Disappearance of 1,10-Phenanthroline Versus Time at 55°C	47
13.	The Rate of Formation of $\text{Pt}(\text{phen})\text{Cl}_2$ in Water Versus $\log [\text{Cl}^-]$ at 55°C	49
14.	The Rate of Formation of $\text{Pt}(\text{phen})\text{Cl}_2$ in Water Versus the Square Root of Ionic Strength at 55°C	50

LIST OF ILLUSTRATIONS--Continued

Figure		Page
15.	The Rate of Disappearance of 1,10-Phenanthroline in 50% Ethanol Versus Time at 55° C	54
16.	The Rate of Formation of Pt(phen)Cl ₂ in 50% Ethanol Versus the Initial Concentration of PtCl ₄ ⁼ at 55° C	57
17.	The Rate of Formation of Pt(phen)Cl ₂ Versus % Ethanol at 55° C	58
18.	The Rate of Disappearance of 1,10-Phenanthroline Versus Time at 45° C in 50% Diglyme	67

LIST OF TABLES

Table		Page
PART I		
I.	THE OBSERVED RATE CONSTANTS FOR THE REACTION OF $\text{Co}_2(\text{CO})_8$ WITH NO UNDER VARIOUS CONDITIONS	17
II.	RATES OF NO EXCHANGE OF SIMPLE METAL NITROSYLS UNDER VARIOUS CONDITIONS	21
III.	THE N-O AND C-O STRETCHING FREQUENCIES IN SOME SELECTED METAL-CARBONYL-NITROSYLS	28
IV.	RELATIVE ABUNDANCES OF THE PRINCIPAL POSITIVE IONS FORMED IN THE MASS SPECTRA OF $\text{Co}(\text{CO})_3\text{NO}$, $\text{Fe}(\text{CO})_2(\text{NO})_2$, AND $\text{Ni}(\text{C}_5\text{H}_5)(\text{NO})$	30
PART II		
V.	THE RATES OF FORMATION OF $\text{M}(\text{phen})_x(\text{H}_2\text{O})_y^{2+}$ AT 25° C	35
VI.	THE RATES OF FORMATION OF SOME COMPLEXES OF NICKEL(II) AT 25° C	37
VII.	SOME RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION $\text{PtCl}_4 \xrightleftharpoons[k_{-1}]{k_1} \text{PtCl}_3\text{H}_2\text{O}^- + \text{Cl}^- \xrightleftharpoons[k_{-2}]{k_2} \text{PtCl}_2(\text{H}_2\text{O})\text{Cl}^-$	40
VIII.	SECOND-ORDER RATE CONSTANTS OF THE REACTION BETWEEN K_2PtCl_4 AND 1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS AND AT A pH OF 2.0 AND IONIC STRENGTH OF 2.3×10^{-2}	46
IX.	SOME SECOND-ORDER REACTION RATE CONSTANTS FOR THE REACTION BETWEEN VARIOUS Pt CONTAINING COMPLEXES AND LIGANDS	51
X.	SOME RATE CONSTANTS FOR THE REACTION BETWEEN K_2PtCl_4 AND 1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS	55
XI.	THE CATALYTIC EFFECT OF VARIOUS MATERIALS ON THE REACTION OF K_2PtCl_4 WITH 1,10-PHENANTHROLINE	62

LIST OF TABLES--Continued

Table		Page
XII	THE OBSERVED RATE CONSTANTS FOR THE ZERO-ORDER REACTION OF K_2PtCl_4 WITH 1,10-PHENANTHROLINE IN MIXED SOLVENT SYSTEMS	65
XIII	RATE CONSTANTS AND % k_0 FOR THE TWO PATHS OF THE REACTION OF $PtCl_4^{2-}$ WITH 1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS	71

ABSTRACT

In Part I of the dissertation the kinetics of nitric oxide exchange of some metal nitrosyls have been measured. The second-order rate constant of nitrosyl exchange at 35° C decreases in the sequence $\text{Fe}(\text{CO})_2(\text{NO})_2$, $3.1 \times 10^{-5} \text{ M}^{-1}\text{-sec}^{-1}$; $\text{Co}(\text{CO})_2\text{NO}$, $7.6 \times 10^{-6} \text{ M}^{-1}\text{-sec}^{-1}$; $\text{Ni}(\text{C}_5\text{H}_6)\text{NO}_2$, $1 \times 10^{-9} \text{ M}^{-1}\text{-sec}^{-1}$. A mechanism involving a trigonal bipyramidal transition state is proposed.

As a preliminary part of the investigation the kinetics of formation of $\text{Co}(\text{CO})_3\text{NO}$ from $\text{Co}_2(\text{CO})_8$ and NO were measured. The first-order formation rate constant was $3.0 \times 10^{-1} \text{ sec}^{-1}$. The rate of reaction was independent of NO concentration but dependent on the concentration of $\text{Co}_2(\text{CO})_8$. The results are discussed in terms of current ideas on the mechanisms of metal-carbonyl reactions.

In Part II of the dissertation the reaction of K_2PtCl_4 and 1,10-phenanthroline to give $\text{Pt}(\text{phen})\text{Cl}_2$ is found to be slow and second-order in water. The second-order rate constant at 55° C is $11.5 \times 10^{-3} \text{ M}^{-1}\text{-sec}^{-1}$. The reaction in mixed solvents such as aqueous ethanol is fast and pseudo-zero-order. The rate constant is independent of the phenanthroline concentration but depends on the initial concentration of K_2PtCl_4 and the concentration of the organic part of the solvent. The results of the aqueous reaction are discussed in terms of the outer-sphere mechanism. For the reaction of K_2PtCl_4 with 1,10-phenanthroline in mixed solvents several possible catalysts are examined, and some mechanisms are proposed in an effort to explain the observed behavior.

PART I

A KINETIC STUDY OF NITROSYL EXCHANGE IN METAL NITROSYLS

CHAPTER 1

INTRODUCTION

Mond and his co-workers prepared the first metal carbonyl, $\text{Ni}(\text{CO})_4$, in 1890 by the direct reaction of nickel metal with carbon monoxide at room temperature and at low pressures (1). It is a clear liquid characterized by a strong odor, instability in air, and extreme toxicity. The structure of $\text{Ni}(\text{CO})_4$ was determined to be tetrahedral by Hieber in 1932 (2).

Until the late 1950's, work on carbonyls and related compounds was sparse and was done mainly by Hieber and his co-workers. Better techniques and new industrial uses spurred interest in these unusual compounds.

Shortly after the discovery of $\text{Ni}(\text{CO})_4$, the isoelectronic compounds $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ were prepared and characterized (2). With the renewed interest in transition metal carbonyls, the preparation of new metal nitrosyl carbonyls also was accelerated. One of the latest to be prepared is $\text{V}(\text{CO})_5\text{NO}$. These compounds are similar to the metal carbonyls, except that for every three carbon monoxides in the parent compound only two nitric oxides are needed to donate the same number of electrons. The fact that nitric oxide is a three-electron donor and a stable free-radical makes it a unique ligand.

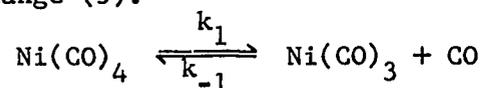
At the present time there is no evidence for compounds containing the neutral free-radical nitric oxide. Compounds formed from

sodium or barium, in liquid ammonia, and nitric oxide were first formulated as anionic nitrosyls, e.g., Na^+NO^- based on an interpretation of IR absorption data. The nitrosyl group absorbs in the 1100 cm^{-1} region and these compounds have an absorption peak in this region. However, these compounds contain, not the nitrosyl ion, but the hyponitrite ion, N_2O_2^- , which also has an absorption in the 1000 cm^{-1} range (3).

The nitrosyl ion, NO^- , absorbs near 1500 cm^{-1} . This has been tentatively identified as the N-O stretching frequency. The observed N-O stretching frequencies in the metal nitrosyls are as follows: $\text{Co}(\text{CO})_3$ 1822 cm^{-1} , 1806 cm^{-1} ; $\text{Fe}(\text{CO})_2(\text{NO})_2$ 1810 , 1767 cm^{-1} ; $\text{V}(\text{CO})_5\text{NO}$ 1700 cm^{-1} ; $\text{Ni}(\text{C}_5\text{H}_5)\text{NO}$ 1820 cm^{-1} . These frequencies are between those of NO^- and NO^+ . Other nitrosyl complexes absorb at lower frequencies down to about 1600 cm^{-1} (3, 4). In this respect, nitric oxide is unusual because very few ligands show such a continuous variation of electron density.

CO Exchange in $\text{Ni}(\text{CO})_4$ and Related Compounds

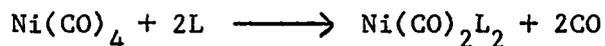
Carbon monoxide exchange with nickel tetracarbonyl in toluene is first order in nickel tetracarbonyl and independent of the carbon monoxide concentration (5). Further, the gas phase thermal decomposition also proceeds by a path independent of the carbon monoxide concentration with an activation energy of more than 12 kcal. This is in good agreement with the activation energy of 13 kcal found for CO exchange in toluene solutions. A simple dissociative mechanism has been proposed for the exchange (5):



Although nickel tetracarbonyl is sterically fairly open to nucleophilic attack, its exchange appears to occur by a dissociative mechanism. The driving force of the reaction may be the better pi bonding that is possible in the trigonal-planar intermediate than in the tetrahedral reactant.

One two of the carbon monoxides may be readily substituted

(6):



Also, in the gas phase decomposition, the first carbon monoxide is lost much more readily than the others (7).

Co(CO)₃NO

Cobalt tricarbonyl nitrosyl is isoelectronic with nickel tetracarbonyl. It behaves much the same in chemical reactions, but all three of the carbon monoxides may be readily substituted (8, 9). The carbon monoxide exchange reaction is first order overall and first order in cobalt tricarbonyl nitrosyl (8). This supports a dissociative mechanism identical with the one proposed for Ni(CO)₄. No evidence was found for substitution of the nitric oxide. This is not unexpected because the metal-nitrogen bond in these compounds is probably much stronger than the metal-carbon bond.

Metal Carbonyls and Phosphorus Trifluoride

The reaction of metal carbonyls and carbonyl nitrosyls with phosphorus trifluoride has been studied (9-13). The behavior of phosphorus trifluoride as a ligand is very similar to that of carbon

monoxide. This is shown in all complexes formed by the reaction of PF_3 with metal carbonyls. Infrared spectra of analogous compounds are very similar, slight shifts of carbonyl bands indicating PF_3 forms slightly stronger bonds than the carbonyl.

No evidence was found for the replacement of the nitric oxide group in the following reaction:



This is not unexpected because PF_3 is in no way similar to NO as a ligand. In addition, the reaction would require the formation of a dimer as the last step, and even if nitric oxide were replaced to form some intermediate, the energetics of the reaction favors the re-formation of the NO complex.

CHAPTER 2

PURPOSE

The purpose of this study is to investigate nitric oxide exchange in some transition metal carbonyl nitrosyl compounds. As a preliminary part of the investigation, the rate of nitric oxide substitution of cobalt octacarbonyl was studied.

CHAPTER 3

EXPERIMENTAL

Synthesis of Cobalt Tricarbonyl Nitrosyl

Cobalt tricarbonyl nitrosyl was synthesized by treatment of the tetracarbonylcobaltate anion with nitric oxide (14).

A one-liter, three-necked flask, fitted with stirrer, dropping funnel, CO and NO inlets, condenser, and gas outlet was charged with a mixture of 160 ml concentrated NH_4OH in 240 ml distilled water. A solution of 17.5 g (0.06 mole) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 40 ml water was added slowly while stirring. Because the intermediate and product are oxygen sensitive, the reaction vessel was cooled to 10°C , and a slight positive pressure of carbon monoxide was maintained.

The dropping funnel, previously filled with a solution of 20 g (0.08 mole) 80% $\text{Na}_2\text{S}_2\text{O}_4$ dissolved in 95 ml concentrated NH_4OH and 135 ml water, was adjusted to deliver one drop every 10 to 15 seconds while the reaction mixture was stirred rapidly and allowed to warm to room temperature.

The reaction mixture was stirred for about 15 minutes after all of the dithionite had been added (about 10 to 12 hours). The condenser was replaced with a short fractionating column connected to a trap cooled in a dry ice-acetone bath. The reaction mixture was treated with a slow stream of nitric oxide for about 15 minutes with rapid stirring and warmed to 48° to 50°C . The nitric oxide was

replaced with nitrogen, and the impure $\text{Co}(\text{CO})_3\text{NO}$ swept into the trap at -79°C .

The cobalt tricarbonyl nitrosyl was purified by vacuum distillations from 0° to -45°C , yielding about 5 g (50%) of product.

Nickel Cyclopentadienyl Nitrosyl

Ten g (0.05 moles) $\text{Ni}(\text{C}_5\text{H}_5)_2$, weighed out under nitrogen in a dry bag, was dissolved in 50 ml pentane under nitrogen and poured into a 100-ml three-necked flask equipped with magnetic stirrer, gas inlet, condenser, and nujol bubbler. Nitric oxide was added slowly -- about one bubble every 10 to 15 seconds -- with stirring until the green solution turned dark red. The solvent was removed by distillation at water pump pressure and the residue was fractionally distilled to give 6 g (80%) of dark red nickel cyclopentadienyl nitrosyl (15).

Cobalt octacarbonyl and iron dicarbonyl dinitrosyl (14) were prepared by standard methods. All other chemicals were purchased as analytical grade reagents from the various chemical companies. N^{15}O was purchased as 99% pure NO gas from the Biorad Laboratories.

Apparatus for NO Substitution

The nitric oxide substitution reactions were carried out in a water-jacketed reaction vessel connected by latex surgical tubing to a variable-path-length, flow-through IR cell and a Teflon circulating pump.

The reaction vessel (Figure 1, p. 10) consisted of two parts. The top, which included a gas inlet, equipped with fitted glass bubbler, a

gas outlet, a solution inlet and outlet, and stopcock with Luer joint used to introduce samples of cobalt octacarbonyl. The bottom, having a water jacket with ball and socket outlets, was connected to the top by a 10-cm O-ring joint.

The Teflon circulating pump was enclosed in a nitrogen-filled polyethylene cover. It was connected to the flow-through cell and the solution return of the reaction vessel by latex surgical tubing.

The system was thermostated using a circulating water bath which regulated the temperature at $0^{\circ} \pm 0.02^{\circ}$ C. The solution was stirred magnetically.

Apparatus for NO Exchange

The nitric oxide exchange reactions were carried out in a glass bulb (Figure 2). The chemical storage and sampling system (Figure 3) consisted of the following: (1) a mechanical vacuum pump connected to (2) a water-cooled mercury diffusion pump to maintain pressure in the 10^{-6} Torr range. The diffusion pump was connected to a manifold made of 20-mm glass tubing which was connected to the storage system through stopcocks 1 and 2. Stopcock 1 connects the manifold to the metal nitrosyl storage bulb, (3) a manometer, and the calibrated volume between and including stopcocks 3 and 4. Stopcock 2 leads to the $N^{15}O$ storage bulb through stopcock 5, another manometer and the calibrated volume used for sample measurement.

All metal nitrosyls were stored at -198° C and 10^{-6} Torr pressure, except when sampling. At that time stopcocks 1 and 2 were closed, thus isolating the storage system from the vacuum pumps. The metal

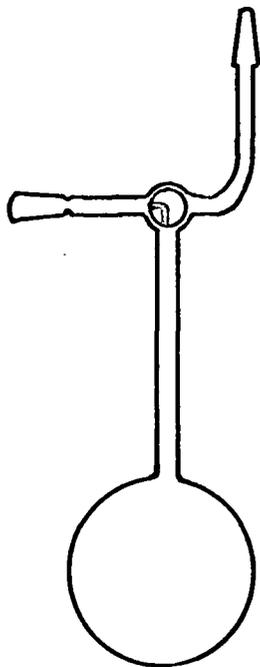


Figure 2. Glass Bulb for the Nitric Oxide Exchange Experiments

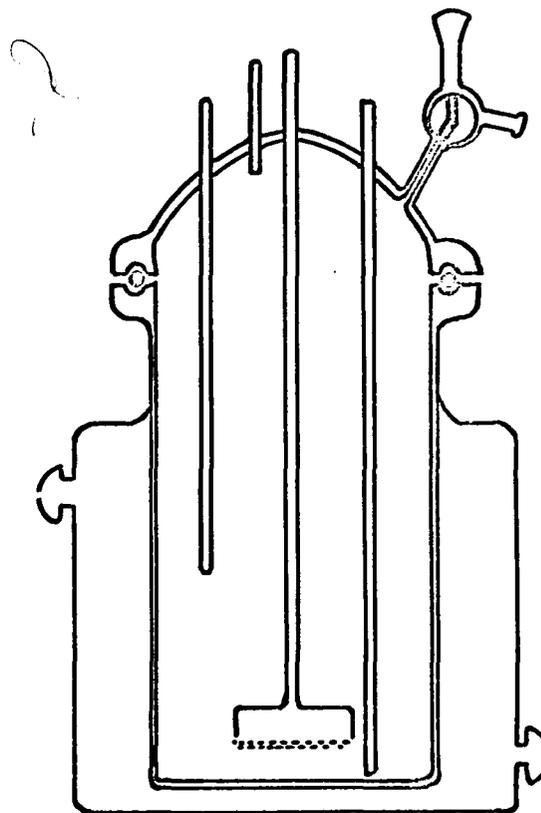


Figure 1. The Reaction Vessel for the Nitric Oxide Substitution Reaction of $\text{Co}_2(\text{CO})_8$

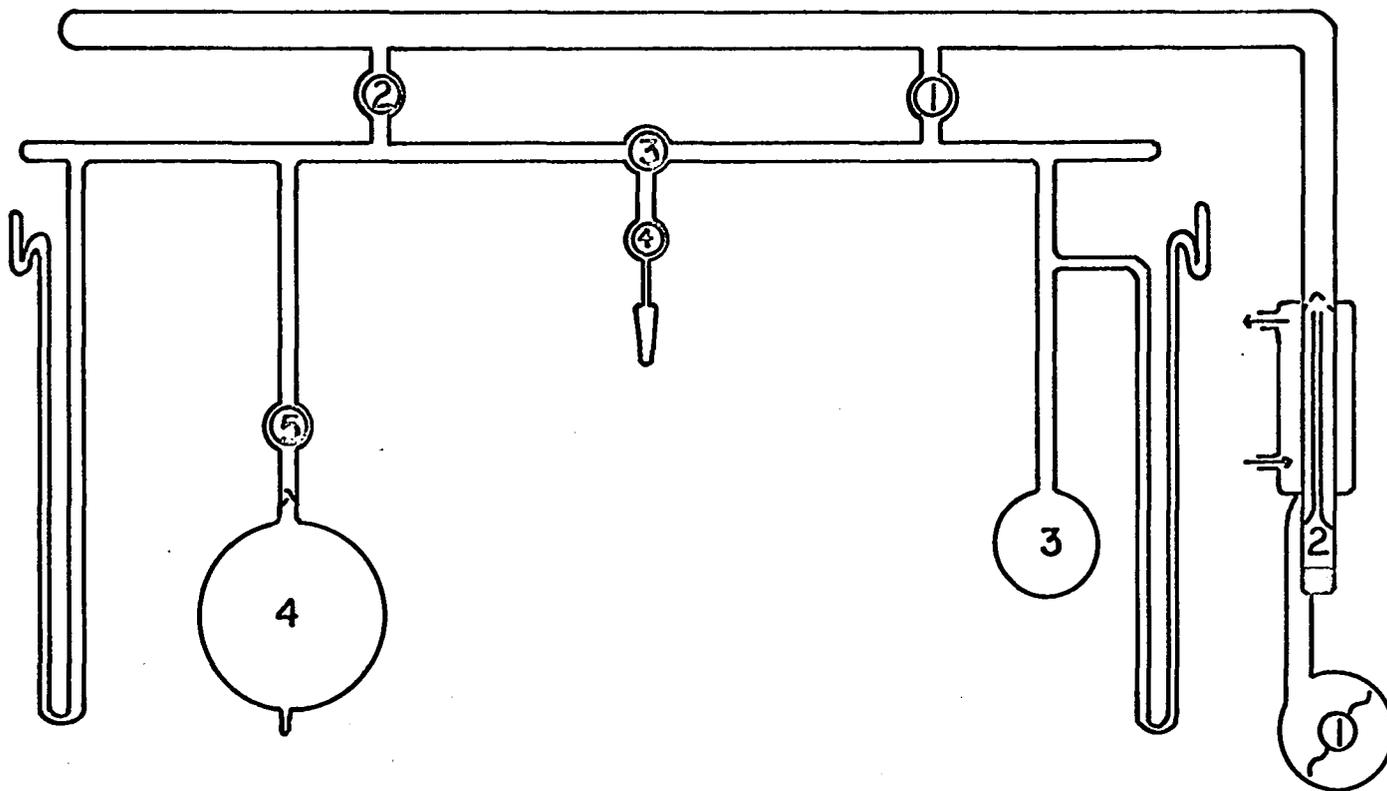


Figure 3. Chemical Storage and Sampling System

Number 1 is the mechanical vacuum pump; 2 is the mercury diffusion pump; 3 is the metal nitrosyl storage bulb and manometer; 4 is the ^{15}NO storage bulb. Stopcocks 1 and 2 connect the manifold to the storage system, 3 and 4 contain a calibrated volume between them, and 5 is used to prevent loss of the ^{15}NO .

nitrosyl was warmed to 25° C and its vapor pressure was measured on the manometer. Stopcock 3 was opened and closed and the trapped metal nitrosyl was condensed into the reaction bulb. This was repeated one or more times until a suitable amount of metal nitrosyl had been condensed into the reaction vessel.

Stopcock 3 was then turned to allow $N^{15}O$ to flow into the sample volume and the procedure was repeated until a suitable sample of $N^{15}O$ was condensed into the reaction vessel.

Substitution Reaction

When the reaction vessel was filled with 120 ml hexane, the water bath circulating pump and Teflon solution pump were turned on. During the several hours that the system was reaching thermal equilibrium, dry nitrogen was passed through to remove air and traces of water. When the solution had reached thermal equilibrium, the nitrogen was shut off and nitric oxide was bubbled into the reaction mixture until the hexane was saturated with nitric oxide.

The absorption maxima at either 1802.4 cm^{-1} (the N-O stretching peak) or 1855 cm^{-1} (the CO bridging peak) were measured using a Beckman IR-4 recording spectrophotometer. A 10-ml sample of a saturated solution of $Co_2(CO)_8$ was injected through the stopcock into the NO saturated hexane and the timer was started. The original concentration of carbonyl was determined from dummy runs without NO. The peak height and extinction coefficient were used to calculate the concentration. Similarly, the concentration of $Co(CO)_3NO$ was determined by taking a reading

at infinite time and calculating the concentration from the extinction coefficient.

N¹⁵O Exchange Reaction

Immediately after the reacting gases had been condensed into the reaction bulb and warmed to room temperature, a small sample, about 3 ml at one cm mercury pressure, was bled into the mass spectrometer to determine the parent and parent-plus-one peak heights. The reaction bulb was then placed in a water bath and new P and P + 1 peaks determined every few days for several weeks.

A minimum of 10 points was determined during the course of the reaction. The change in the P : P + 1 ratio was from about 25 : 1 to about 4 : 1 for all of the nitrosyls.

Determination of the Rate Constants in the Exchange Reaction

At set times during the course of a kinetic run, the parent, P + 1, and P : P + 1 ratios were recorded. From these data and from the original concentration of gases determined from the manometer readings and sampling volume, it was possible to determine the number of moles of $\text{Co}(\text{CO})_3\text{N}^{15}\text{O}$ formed in the course of a reaction.

The original metal nitrosyl contains some N¹⁵O as shown by the P + 1 peak at t = 0. Since the ratio of P : P + 1 must be equal to the ratio of $[\text{M}(\text{NO})] : [\text{M}(\text{N}^{15}\text{O})]$, it is possible to calculate the number of moles of M(NO) and MN¹⁵O at t = 0 and at any time.

All of the exchange reactions were found to follow the McKay (16) equation and give linear plots of $\log (C_0 - C_\infty / C - C_\infty)$ versus time.

Where C_0 is the initial concentration of metal nitrosyl, C is the concentration at time t , and C_{∞} is the equilibrium concentration. The apparent rate constant is equal to the slope of this line multiplied by 2.303. The apparent rate constant is related to k_{true} by the equation: $k_{\text{true}} = k_{\text{apparent}} \frac{Xa^{1-\alpha} b^{1-\beta}}{Xa + b}$ where a is the concentration of metal nitrosyl, α is the order in a , b is the NO concentration, β is the order in b , and X is the number of exchangeable NO's in the nitrosyl.

Determination of the Rate Constants in the
Substitution Reaction of NO on $\text{Co}_2(\text{CO})_8$

During the course of a kinetic run, the time required for the chart to move one division (1 cm) was recorded. The change in concentration was automatically recorded by the machine. Even at 0° C the reaction was extremely rapid with only about 30 seconds required to use up all of the NO in solution. First-order plots of the data gave straight lines. No change in rate was observed with changes in NO concentration. However, because of the rapidity of the reaction, results are probably good only to a factor of 2 or 3.

CHAPTER 4

RESULTS

The Substitution Reaction of $\text{Co}_2(\text{CO})_8$ by NO

When a solution of $\text{Co}_2(\text{CO})_8$ in hexane was added to a solution of NO in hexane, a reaction occurred forming CO and $\text{Co}(\text{CO})_3\text{NO}$ at a first-order rate. Mass spectra and infrared analysis showed only $\text{Co}(\text{CO})_3\text{NO}$ and CO as final products. When a small amount of air was present in the reaction mixture, a dark brown solid product containing Co, CO, NO, and NO_2 was noticed. Infrared spectra of this compound indicated that the NO_2 was acting as a bridging ligand presumably between two cobalt atoms. No bridging carbonyl peaks were observed.

From plots such as Figure 4 the rate of substitution at 0°C was determined to be $2.0 \pm 1.0 \times 10^{-2} \text{sec}^{-1}$ over a threefold change in concentration of both reactants (Table I). This first-order reaction was independent of NO concentration. The exchange of CO in $\text{Co}_2(\text{CO})_8$ is first-order in complex and independent of the CO concentration. The rate of exchange at $+5^\circ \text{C}$ is $2.5 \times 10^{-3} \text{sec}^{-1}$ (5). Infrared solution spectra show that there is a rapid equilibrium between carbonyl bridged and unbridged forms of cobalt octacarbonyls (17). Two mechanisms have been proposed to account for these results. The first (5), Figure 5a, involves the breaking of one of the carbonyl bridges and attack, by carbon, at the Co with the fewer CO's. The second (5, 18), Figure 5b, involves the formation of a biradical intermediate and the breaking of

Figure 4. The Rate of Disappearance of $\text{Co}_2(\text{CO})_8$ in Hexane versus Time at 0°C

The concentration of $\text{Co}_2(\text{CO})_8$ calculated from the rate of appearance of $\text{Co}(\text{CO})_3\text{NO}$ in hexane at 0°C .

The initial concentration of $\text{Co}_2(\text{CO})_8 = 9.0 \times 10^{-3} \underline{\text{M}}$

$\text{NO} = 2.0 \times 10^{-3} \underline{\text{M}}$

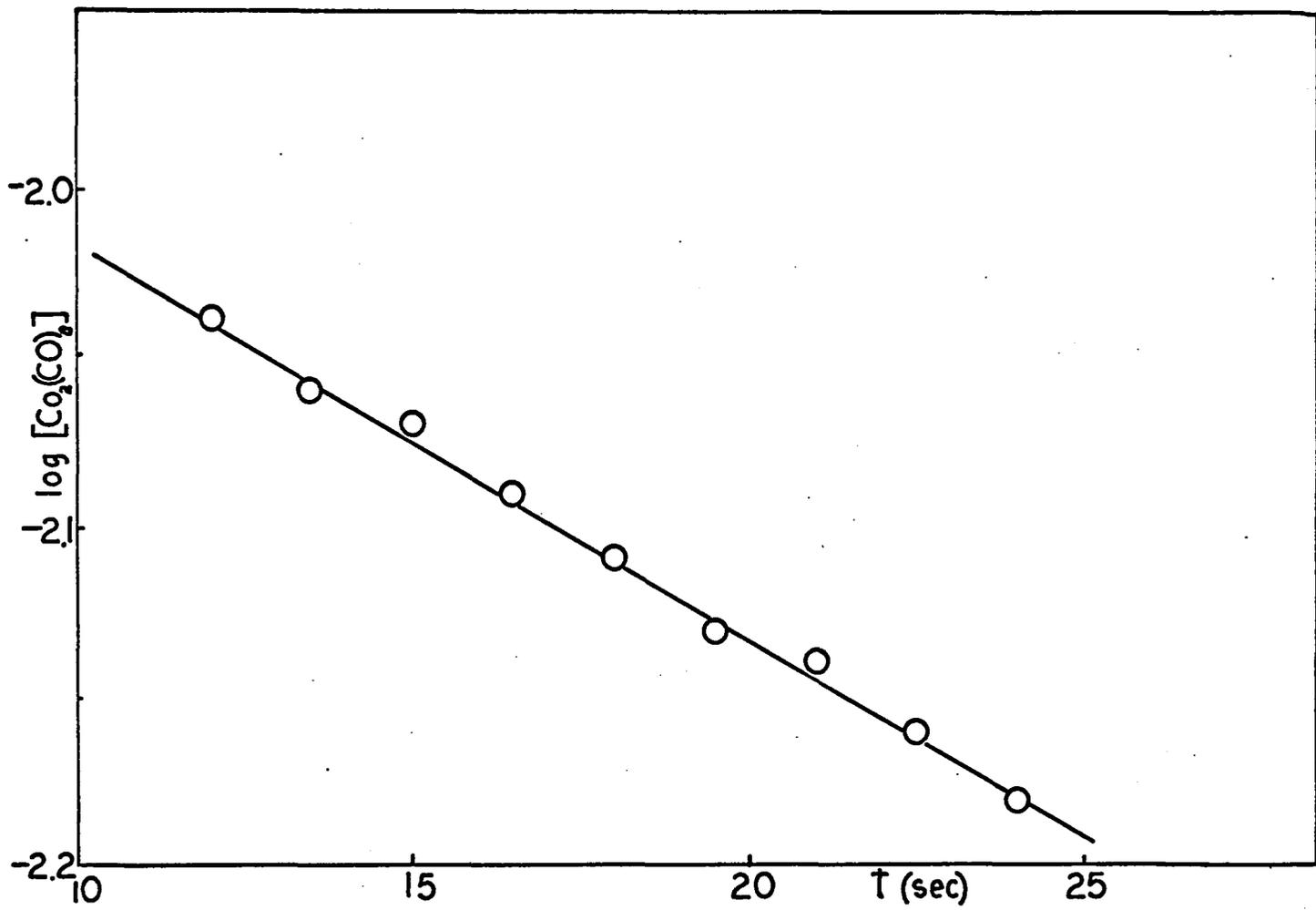


Figure 4. The Rate of Disappearance of $\text{Co}_2(\text{CO})_8$ in Hexane versus Time at 0°C

TABLE I
 THE OBSERVED RATE CONSTANTS FOR THE REACTION OF $\text{Co}_2(\text{CO})_8$
 WITH NO UNDER VARIOUS CONDITIONS

$10^3 \times [\text{Co}_2(\text{CO})_8](\underline{\text{M}})^a$	$10^3 \times [\text{NO}](\underline{\text{M}})^a$	T° C	$10^1 \times k_{\text{obs}}(\text{sec}^{-2})$
9.0	2.0	0° C	2.0 ± 1
9.0	0.50	0° C	1.4
9.0	2.1	5° C	40 ± 10^b
4.5	2.0	0° C	3.0 ± 1.0
2.2	2.0	0° C	27^b
0.9	2.0	0° C	20^b

a. In hexane solutions

b. Calculated from the rate of disappearance of cobalt octa-carbonyl

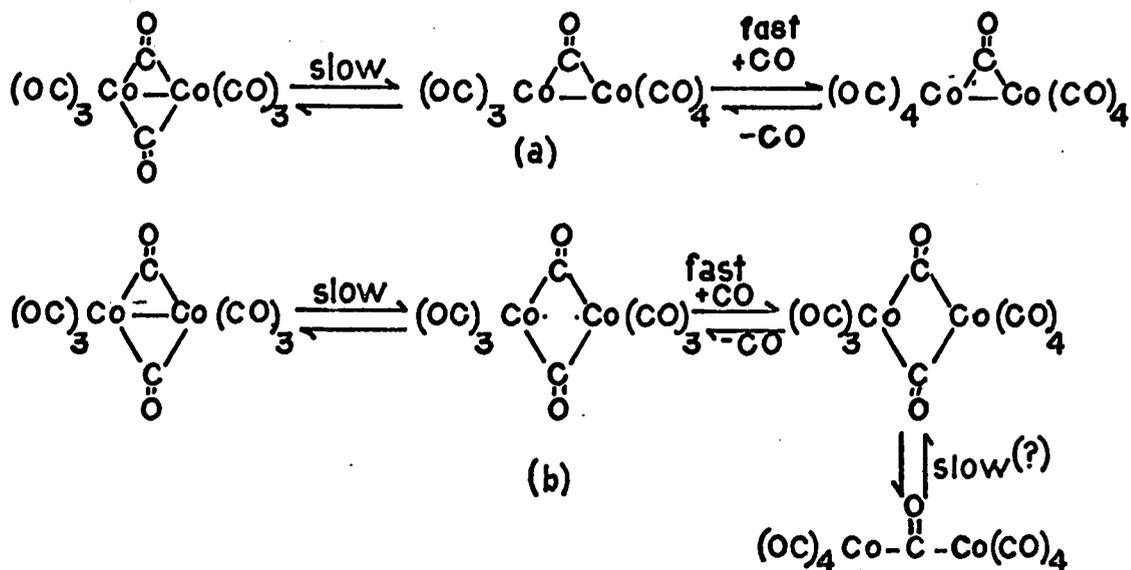


Figure 5. Possible Mechanisms for CO Exchange in $\text{Co}_2(\text{CO})_8$

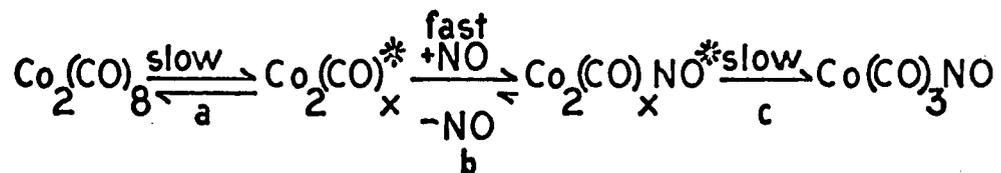


Figure 6. Possible Mechanisms for the NO Substitution of $\text{Co}_2(\text{CO})_8$

one of the carbonyl bridges. Both mechanisms satisfactorily explained the data on CO exchange. A different mechanism has been proposed for the substitution reaction of $\text{Co}_2(\text{CO})_8$ by $\text{P}(\text{Ph})_3$ (8). This mechanism involves the rapid formation of an intermediate and its slow decomposition to product.

The rate determining step in the NO substitution reaction must be different from the rate step in the exchange reaction because the first was about 100 times faster than the second. The rate of disappearance of $\text{Co}_2(\text{CO})_8$ is very near the rate found in the $\text{P}(\text{Ph})_3$ substitution reaction. It seems reasonable to propose a mechanism involving the formation of several intermediates and their decomposition to the final products. Other mechanisms may be cited but until the details of the reaction are known, such speculation is futile.

The Exchange Reaction of $\text{Co}(\text{CO})_3\text{NO}$ with ^{15}NO

When $\text{Co}(\text{CO})_3\text{NO}$, in the gas phase, was mixed with ^{15}NO , the nitric oxide was exchanged to form $\text{Co}(\text{CO})_3^{15}\text{NO}$ and NO at a constant rate. Figure 7 is a kinetic plot of the exchange of $\text{Co}(\text{CO})_3\text{NO}$ from which the apparent rate constants were determined. Some decomposition of the $\text{Co}(\text{CO})_3\text{NO}$ was observed during the course of the reaction but this did not seem to affect the rate of exchange.

The apparent first-order rate constants and the related second-order rate constants under various reaction conditions are listed in Table II. Figure 8 is a plot of the first-order rate constant versus NO . It is apparent that there is a first-order rate-dependence on the concentration of the ^{15}N -nitric oxide. This suggests that nitric oxide exchange, unlike carbon monoxide exchange, reacts through an associative

Figure 7. The Rate of Nitric Oxide Exchange of $\text{Co}(\text{CO})_3\text{NO}$ Versus Time at 35°C

The initial concentration of $[\text{Co}(\text{CO})_3\text{NO}] = 3.58 \times 10^{-4} \text{M}$;
 $[^{15}\text{NO}] = 3.65 \times 10^{-4} \text{M}$.

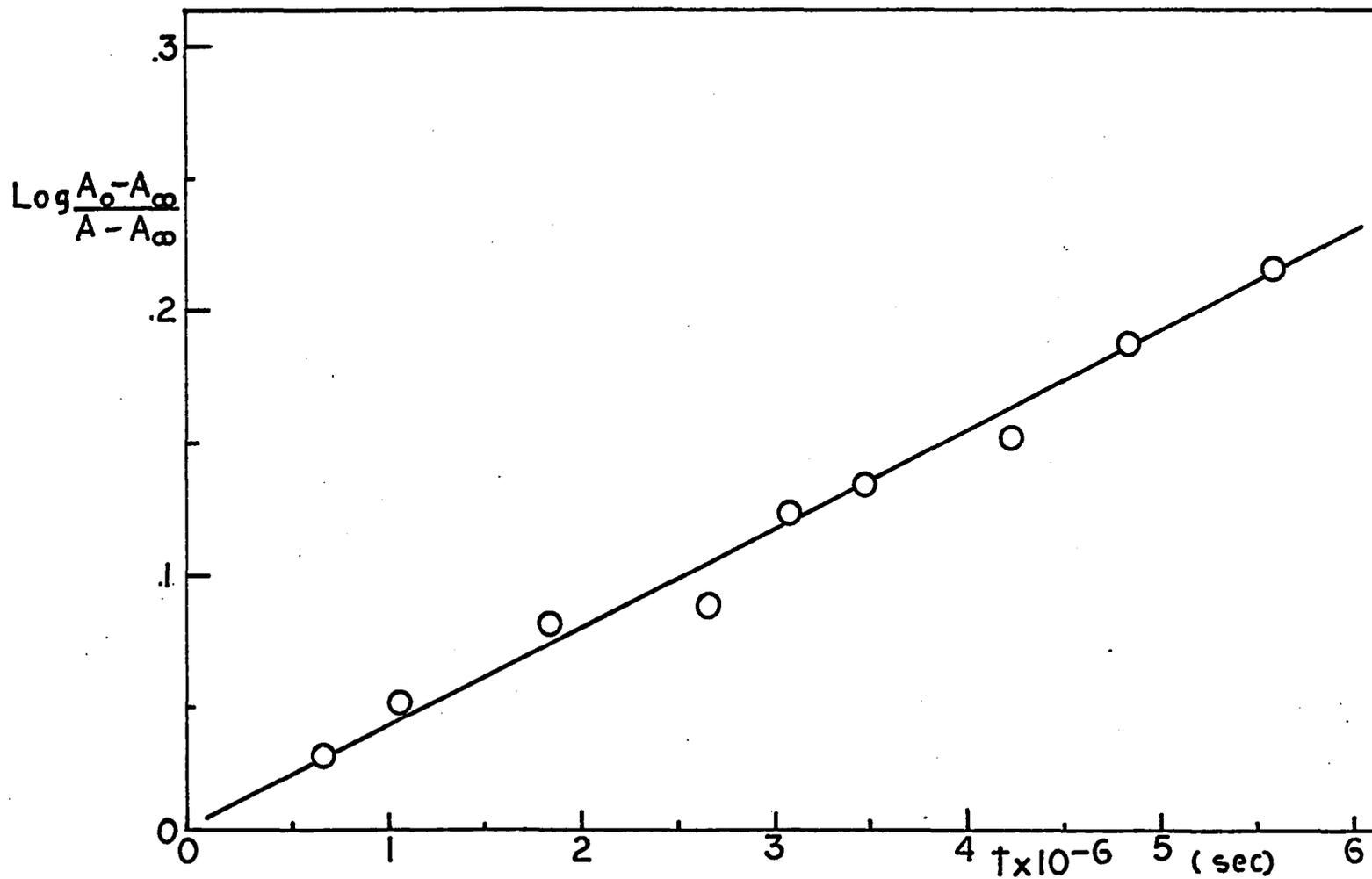


Figure 7. The Rate of Nitric Oxide Exchange of $\text{Co}(\text{CO})_3\text{NO}$ Versus Time at 35°C

TABLE II
 RATES OF NO EXCHANGE OF SIMPLE METAL NITROSYLS
 UNDER VARIOUS CONDITIONS

Complex	$10^4 \times [\text{complex}]^a$	$10^4 [\text{NO}]^a$	T° C	$10^8 \times k_{\text{app}}^b$	$10^6 \times k_{\text{true}}^c$
Co(CO) ₃ NO	4.25	5.70	25	8.0	4.1 ± 0.2
	3.66	4.11		4.5	
	4.10	4.05		6.0	
	3.91	4.14	35	11.8	7.6 ± 0.14
	2.14	3.72		8.7	
	2.48	4.39		10.4	
	3.58	3.65		11.1	
	4.18	2.08		9.5	7.6 ± 0.2^d
	3.70	2.07		8.8	
	3.48	4.43		19.3	8.0 ± 0.14^e
	4.16	2.20		9.8	
Fe(CO) ₂ (NO) ₂	1.90	3.57	25	14.4	18.0 ± 2.0
	1.53	3.41		12.8	
	2.08	2.14		13.7	
	2.25	2.08	35	19.0	31.0 ± 2.0
	3.71	2.12		28.2	
	3.53	3.82		32.0	
	3.04	3.67		29.3	
	3.50	3.74		31.5	30.0 ± 1.0^d
	3.61	6.48		40.0	
	2.05	5.40		27.4	33.0 ± 1.0^e
	4.42	3.78		39.1	
	4.05	3.63		32.0	
	3.68	3.65		36.7	
Ni(C ₅ H ₅)(NO)	7.00	3.41	45	0.1	
	7.00	3.41	120	0.01	

a. Moles, volume 50 ± 1 ml

b. First-order rate constant (sec^{-1})

c. Second-order rate constant ($\text{M}^{-1}\text{-sec}^{-1}$)

d. Reaction run with a carbon monoxide concentration = $5 \times 10^{-3} \text{M}$

e. Run in reaction vessels partly filled with glass beads, volume 35 ± 1 ml

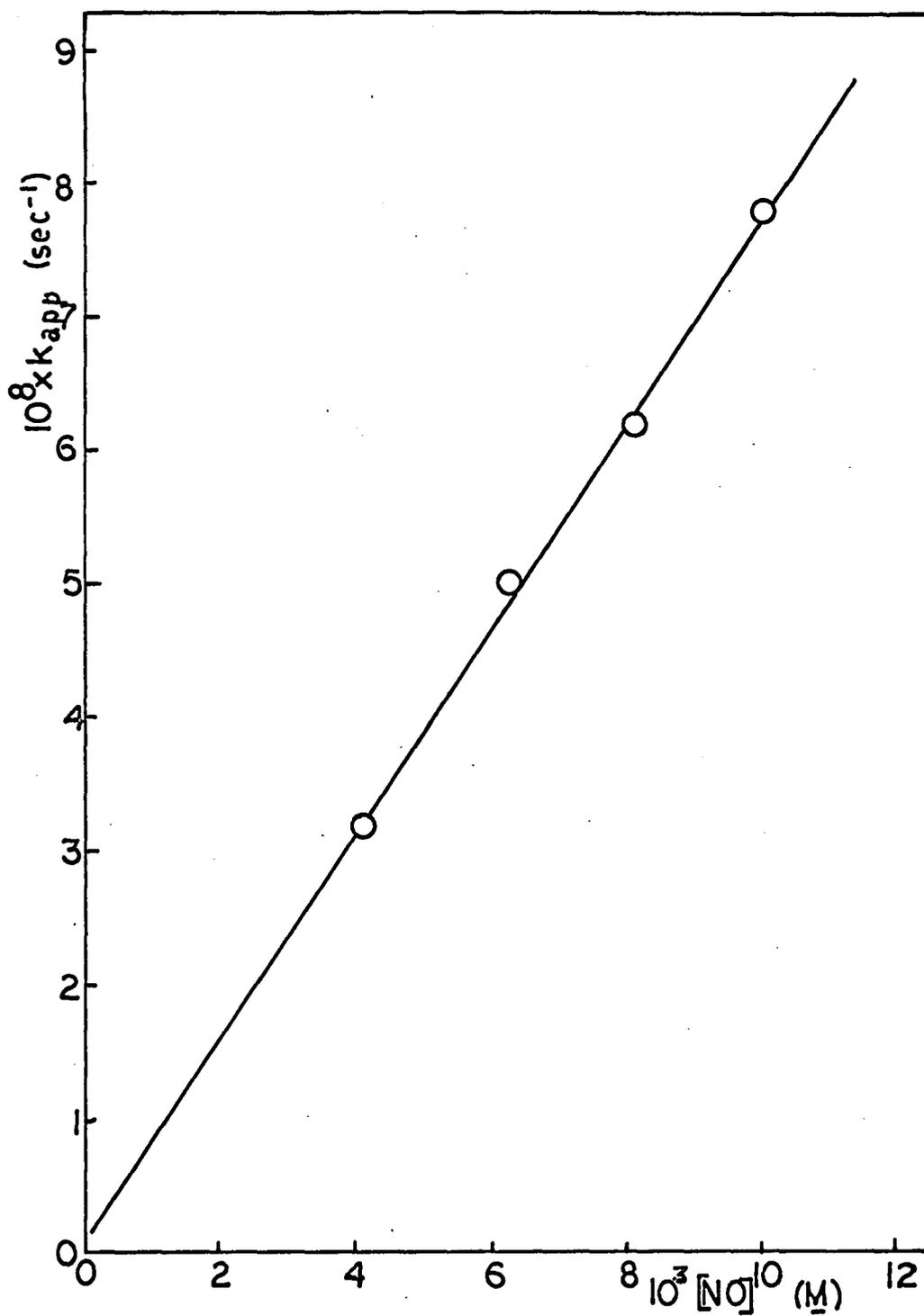


Figure 8. The First-order Rate of Nitric Oxide Exchange of $\text{Co}(\text{CO})_3\text{NO}$ Versus the Concentration of ^{15}NO
The initial concentration of $[\text{Co}(\text{CO})_3\text{NO}] = 3.5 \times 10^{-4} \text{ M}$.

mechanism. The rate was independent of the concentration of carbon monoxide. Catalysis by the wall of the reaction vessel was examined by filling reaction vessels about one-half full of 4-mm glass beads prior to a reaction run. No significant change in the rate of reaction was observed although the available wall surface was increased by at least a factor of five.

The Exchange Reaction of $\text{Fe}(\text{CO})_2(\text{NO})_2$ with ^{15}NO

Exchange between $\text{Fe}(\text{CO})_2(\text{NO})_2$ and ^{15}NO behaved in the same manner as the $\text{Co}(\text{CO})_3\text{NO}$ - ^{15}NO reaction. The apparent first-order rate constants and the related second-order rate constants are listed in Table II.

These show that the rate was again dependent on the concentration of both reactants. In the same manner, excess CO caused no change in the rate of the reaction. Wall effects were again negligible.

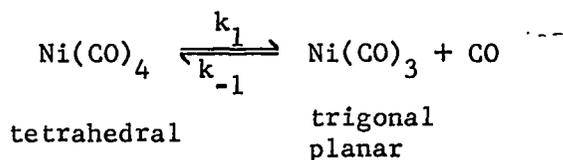
The Exchange Reaction of $(\text{C}_5\text{H}_5)\text{Ni}(\text{NO})$ with ^{15}NO

An attempt was made to study the rate of exchange of ^{15}NO with the molecule $(\text{C}_5\text{H}_5)\text{Ni}(\text{NO})$ which was isoelectronic with, and structurally similar to $\text{Co}(\text{CO})_3\text{NO}$. After 30 days at 45°C , no exchange had been observed. After 10 days at 120°C , no exchange had occurred although some decomposition was observed. The rate of exchange of nitric oxide with $(\text{C}_5\text{H}_5)\text{Ni}(\text{NO})$ was much slower than the rate of exchange of the $\text{Co}(\text{CO})_3\text{NO}$ or $\text{Fe}(\text{CO})_2(\text{NO})_2$. No further work was attempted.

CHAPTER 5

CONCLUSIONS

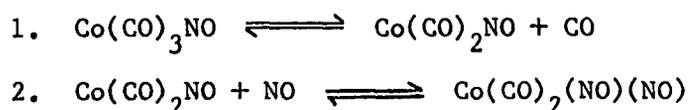
The carbon monoxide exchange with simple metal-carbonyl complexes has been studied thoroughly (5, 8). In all of the reactions so far studied, the rate of exchange was dependent on the metal complex concentration and independent of the concentration of carbon monoxide. The mechanism proposed (shown here for $\text{Ni}(\text{CO})_4$) is:



It has been calculated (19) that there are two orbitals available on the metal to pi bond with the vacant p orbitals of the ligand in the tetrahedral structure, while in the trigonal structure there are three. Thus, the driving force for the proposed mechanism might be the stabilization effect of pi bonding in the trigonal transition state.

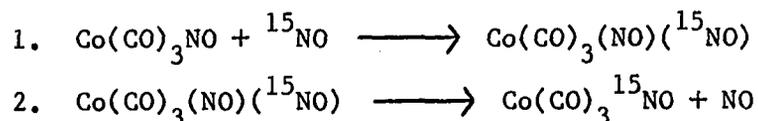
Several mechanisms present themselves as possibilities for the exchange of NO in the metal nitrosyls discussed in this paper. The first is the simple dissociative mechanism found in the carbon monoxide exchange. However, such a mechanism is first-order in only the metal complex. In the nitric oxide exchange the rate was dependent on both the NO and the metal complex.

Another possibility might be a modification of the dissociative mechanism:



This mechanism would show a first-order dependence in both NO and $\text{Co}(\text{CO})_3\text{NO}$. However, this mechanism predicts that introduction of excess CO would cause a decrease in the metal nitrosyl available to react with the nitric oxide, thereby decreasing the rate. Such a result was not observed and added CO did not affect the rate of reaction.

A third mechanism might be:



The first step is the formation of a five-coordinate complex as either an intermediate or a transition state. In step two this five-coordinate complex would lose one molecule of nitric oxide regenerating the original compound. This rate of exchange following such a scheme would be second-order, first-order in complex, and first-order in nitric oxide. Such a scheme would not show a rate dependence on carbon monoxide. Also this mechanism requires no heterogeneous catalysis; wall effects would not play a role in the reaction.

The great majority of exchange reactions involving radicals have ΔH^* values in the range 5 to 12 kcal/mole, while the great majority of reactions which follow a dissociative mechanism have ΔH^* values of 12 to 60 kcal/mole (20, 21). Thus the low heat of activation, 9.3 kcal/mole for $\text{Co}(\text{CO})_3\text{NO}$, 7.6 kcal/mole for $\text{Fe}(\text{CO})_2(\text{NO})_2$, is

consistent with a bimolecular gas phase reaction. The very low entropy of activation suggests that both the entering and leaving NO groups are relatively far from the central metal. Three possible structures of such a transition state are shown for $\text{Co}(\text{CO})_3(\text{NO})_2$ in Figure 9. The intuitive choice of a structure of a transition state would be the trigonal bipyramidal structure. Such a structure would allow the entering ligand to assist exchange by forcing the leaving ligand far from the molecule. Evidence more concrete than an intuitive feeling is available in support of trigonal bipyramidal transition state. No exchange was observed in the molecule $\text{Ni}(\text{C}_5\text{H}_5)\text{NO}$. This molecule is structurally similar to the tetrahedral molecules $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$. In the nickel compound three of the ligands have been replaced by the cyclopentadienyl ring. All three compounds are isoelectronic at least to a first approximation. Therefore, the behavior of the three molecules should be similar. The iron and cobalt compounds do behave in much the same manner toward NO exchange, while the nickel compound's behavior is much different. The proposed mechanism involving the trigonal bipyramidal transition state explains this behavior. While any three of the ligands in the iron and cobalt complexes are free to move up through a plane containing the metal atom and three ligands, such a movement is not possible in the nickel complex. The cyclopentadienyl ring is not large enough to pass over the metal atom; therefore, it cannot form the required transition state. Exchange would require either a dissociative mechanism or an associative mechanism involving a transition state in which both nitric oxides are on the same side of the molecule.

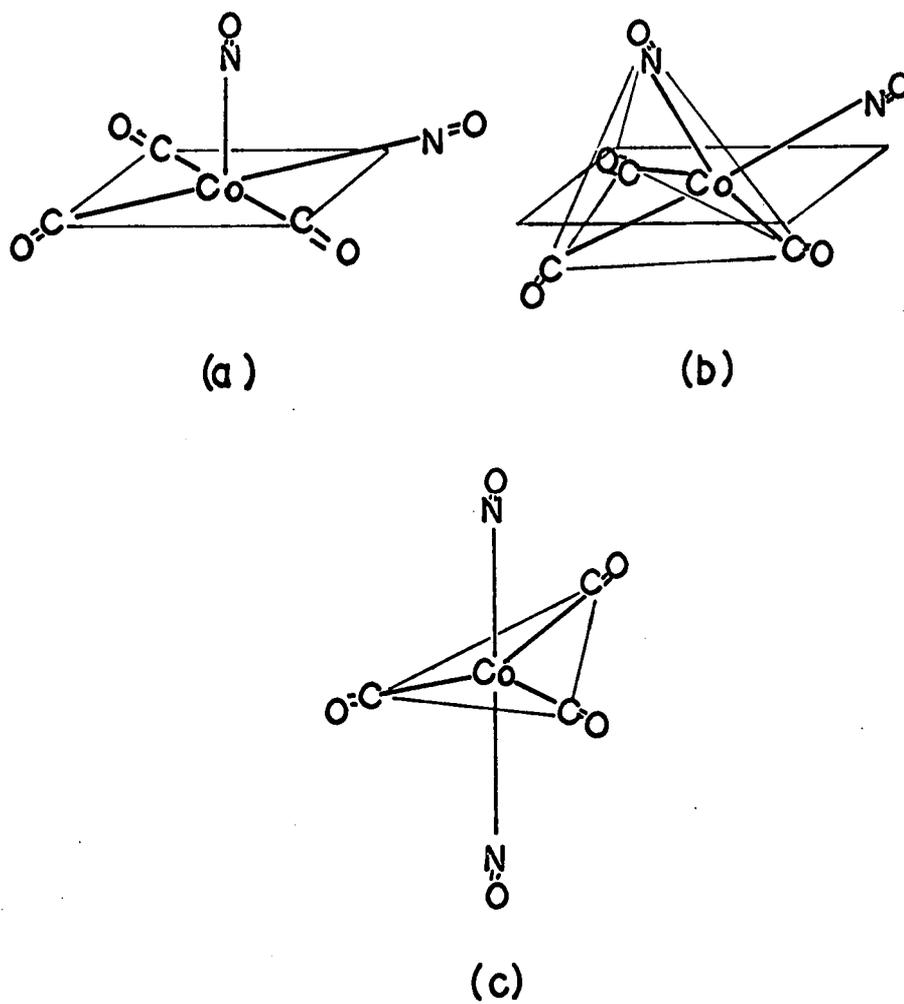


Figure 9. Possible Structures of $\text{Co}(\text{CO})_3(\text{NO})_2$

The order of reactivity of $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3\text{NO}$, and $\text{Fe}(\text{NO})_2(\text{CO})_2$ in the carbon monoxide exchange reaction is inversely related to the degree of nitric oxide substitution (22). This difference is more than a statistical one as the relative rates were approximately $\text{Fe}(\text{CO})_2(\text{NO})_2$, 1; $\text{Co}(\text{CO})_3\text{NO}$, 36; $\text{Ni}(\text{CO})_4$, 3000. The conclusion was that inclusion of NO strengthens the CO-metal bonds, thereby decreasing the rate of dissociation. Just the opposite results were obtained in the study of the nitric oxide exchange. Here the iron-dicarbonyl-dinitrosyl exchanged about five times faster than the cobalt-tricarbonyl-nitrosyl. If the conclusion made in the carbonyl-carbon monoxide work is correct, then the inclusion of more than one nitric oxide into a molecule weakens the metal-nitric oxide bond. An examination of the C-O and N-O stretching frequencies (3) seems to bear out these suppositions (Table III).

TABLE III
THE N-O AND C-O STRETCHING FREQUENCIES IN SOME SELECTED
METAL-CARBONYL-NITROSYLS

Complex	C-O (cm^{-1})	N-O (cm^{-1})
$\text{V}(\text{CO})_5(\text{NO})$	2108	1700
$\text{Mn}(\text{CO})_4(\text{NO})$	2095	1759
$\text{Co}(\text{CO})_3(\text{NO})$	2100	1806
$\text{Fe}(\text{CO})_2(\text{NO})_2$	2084	1810
$\text{Mn}(\text{CO})(\text{NO})_3$	2008	1823
$(\text{C}_5\text{H}_5)\text{NiNO}$		1820

As the ratio of NO to CO increases, the CO stretching frequency decreases, indicating stronger bonding between the carbon and the metal. At the same time the N-O stretch increases, indicating a stronger N-O bond and hence a weaker metal-nitrogen bond. The mass spectra of the three compounds (Table IV) add further evidence in favor of the assumption that the more NO's the weaker the metal-nitrogen bond and the stronger the metal-carbon bond. The relative abundances of the ions having lost a NO are much higher in $\text{Fe}(\text{NO})_2(\text{CO})_2$ than in the $\text{Co}(\text{CO})_3\text{NO}$. This supposition may be tested by preparing the next compound in the series, $\text{Mn}(\text{NO})_3\text{CO}$, and determining the rate of exchange of nitric oxide. It should exchange faster than the iron compound. The $\text{Mn}(\text{CO})(\text{NO})_3$ does not have a high enough vapor pressure to allow an examination of the gas phase kinetics and the compound in the gas phase exists in equilibrium with $\text{Mn}(\text{NO})(\text{CO})_4$. However, if examinations of the exchange of nitric oxide with metal nitrosyls in solution follows a similar path to the gas phase exchange, then it may be possible to study the manganese-carbonyl-trinitrosyl, adding further evidence for the proposed mechanism.

TABLE IV

RELATIVE ABUNDANCES OF THE PRINCIPAL POSITIVE IONS FORMED IN THE
 MASS SPECTRA OF $\text{Co}(\text{CO})_3\text{NO}$, $\text{Fe}(\text{CO})_2(\text{NO})_2$, AND $\text{Ni}(\text{C}_5\text{H}_5)(\text{NO})$

Ions	$\text{Co}(\text{CO})_3(\text{NO})$	$\text{Fe}(\text{CO})_2(\text{NO})_2$	$\text{Ni}(\text{C}_5\text{H}_5)(\text{NO})$
M^+	100	100	12
$\text{M}(\text{CO})^+$	99	85	
$\text{M}(\text{NO})^+$	10	23	2
$\text{M}(\text{CO})_2^+$	19	68	
$\text{M}(\text{CO})(\text{NO})^+$	10	7	
$\text{M}(\text{NO})_2^+$		4	
$\text{M}(\text{CO})_3^+$	0		
$\text{M}(\text{CO})_2(\text{NO})^+$	43	2	
$\text{M}(\text{CO})(\text{NO})_2^+$		19	
$\text{M}(\text{CO})_3(\text{NO})$	12		
$\text{M}(\text{CO})_2(\text{NO})_2^+$		11	
$\text{M}(\text{C}_5\text{H}_5)$			100
$\text{M}(\text{C}_5\text{H}_5)(\text{NO})$			40
$\text{M}(\text{CO})^{++}$	7		
$\text{M}(\text{CO})_2^{++}$	6		
$\text{M}(\text{C}_5\text{H}_5)(\text{NO})^{++}$			2

PART II

A KINETIC STUDY OF THE REACTION OF VARIOUS ORTHO-PHENANTHROLINES
WITH POTASSIUM TETRACHLOROPLATINATE II

CHAPTER 1

INTRODUCTION

The compound 1,10-phenanthroline (Figure 10) was first prepared by Blau in 1897 (23). When 1,10-phenanthroline was mixed with salts of iron(II) or (III), it formed colored compounds of the general formula $\text{Fe}(\text{phen})_3\text{X}_2$ or $\text{Fe}(\text{phen})_3\text{X}_3$. The formation of these compounds was inexplicable by the structural theory of molecules of that time. However, according to the new Werner (24) theory of formation and reaction of metal complexes, the formation and reactions of the iron--1,10-phenanthroline complexes were straightforward and characteristic.

The compound 1,10-phenanthroline and its substituted derivatives are bidentate ligands, coordinating through the nitrogens to form five-membered rings. The chelate ring containing the metal atom is coplanar with the rest of the phenanthroline molecule. Ligands of particular interest are 1,10-phenanthroline and substituted 1,10-phenanthroline. Complexes of 1,10-phenanthroline are formed with metals from all groups (25) except the rare earth elements, and although phenanthroline is a relatively weak base, it forms extremely stable complexes with these metals in many different oxidation states. The simple functional grouping $\text{C} = \text{N} - \text{C} - \text{C} - \text{N} = \text{C}$ alone does not account for this behavior. Nyholm (26, 27) has proposed that the major factor responsible for the strong bonding in many of the iron triad complexes is the formation of double bonds to give resonance forms illustrated by Figure 11.

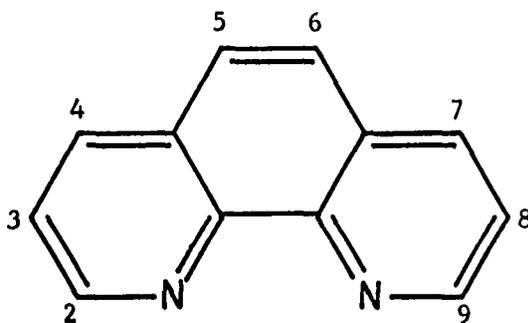


Figure 10. The Structure of 1,10-Phenanthroline

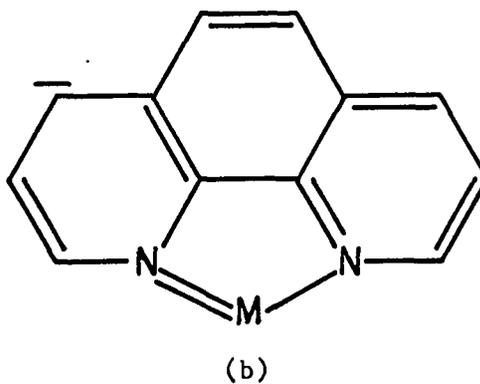
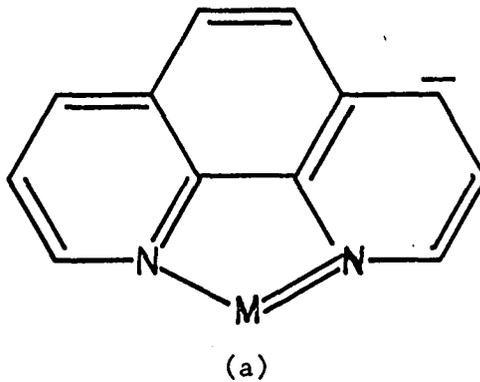


Figure 11. The Suggested Resonance Forms of 1,10-Phenanthroline-metal Complexes

Recent NMR and EPR studies (28, 29, 30) show that the 1,10-phenanthroline molecule is aromatic. The EPR study also showed that electrons from a metal atom bonded to phenanthroline are delocalized over the phenanthroline (28). Pi bonding is often used to explain the stability of complexes formed by metals at low oxidation states. The EPR results are direct evidence of this type of bonding.

All metals of the nickel triad can be coordinated by 1,10-phenanthroline (31-37). Nickel(II) forms complexes containing from one to three 1,10-phenanthrolines; the $\text{Ni}(\text{phen})_3^{+2}$ is the most stable of the complexes (31, 32). Platinum(II) and palladium(II) are usually four-coordinate and therefore may form compounds containing one or two phenanthrolines (33, 34). The monosubstituted complexes $\text{M}(\text{phen})\text{X}_2$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , SCN^- , etc.) have been prepared and are sparingly soluble (35, 36, 37).

Substitution Reactions of Transition Metal Complexes with 1,10-Phenanthroline

The formation constants in aqueous solution of most of the complexes of phenanthroline are known. The ligands have absorption maxima with large extinction coefficients in the near ultraviolet, and these absorptions are shifted to different wavelengths in their complexes. The complexes are extremely stable so that even micromolar solutions of a metal and the ligand react to form complexes containing one or more phenanthrolines. For these reasons 1,10-phenanthroline and substituted 1,10-phenanthrolines are often used in studies of the kinetics of substitution reactions of transition metal complexes.

The Substitution Reactions of Some Transition Metals
at a +2 Oxidation State with 1,10-Phenanthroline

The rate of formation of complexes of phenanthroline and transition metals at an oxidation state of +2 seems to be controlled by the water exchange rate of the aquated metal ion or complex (38-42). The second-order rate constant (k_f) for the formation of many metal complexes seems to be the product of a first-order rate constant, k_1 for water exchange, and an outer sphere association constant, K_o , i.e., $k_f = K_o k_1$. In the formation of a chelate complex with a metal at a +2 oxidation state, the rate of formation is usually controlled by the rate of release of the first water molecule from the metal ion (40, 42).

The formation rate constants for $M(\text{phen})_x(\text{H}_2\text{O})_y^{2+}$ are collected in Table V. In the reaction with phenanthroline the order of reactivity is $\text{Ni}^{\text{II}} > \text{Co}^{\text{II}} > \text{Fe}^{\text{II}} > \text{Zn}^{\text{II}} > \text{Cu}^{\text{II}} > \text{Cd}^{\text{II}} > \text{Hg}^{\text{II}}$. This parallels the sequence observed for the water exchange rate and also the rates of formation of complexes with bipyridine, oxalate, EDTA, glycine, etc. (38-42).

TABLE V

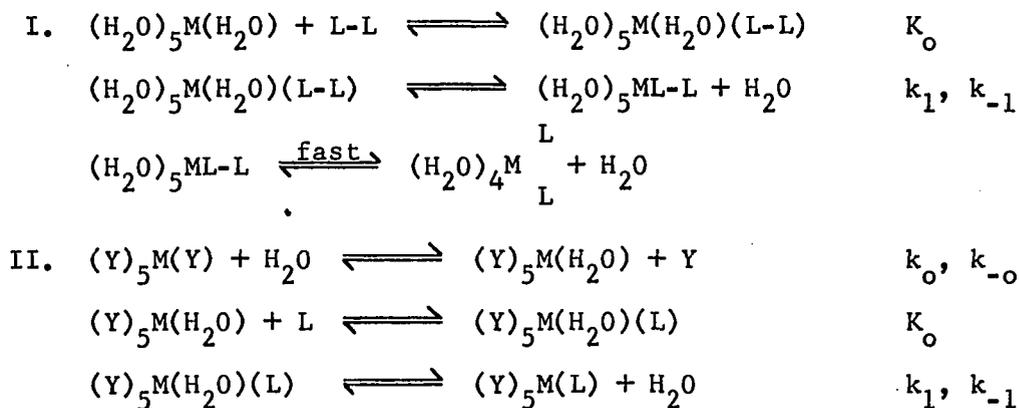
THE RATES OF FORMATION OF $M(\text{phen})_x(\text{H}_2\text{O})_y^{2+}$ AT 25° C (42)

Ion	Log k_f^a
Fe ²⁺	5.2
Co ²⁺	5.5
Ni ²⁺	3.5
Cu ²⁺	7.0
Zn ²⁺	6.3
Cd ²⁺	7.0

a. Formation rate constant ($\text{M}^{-1}\text{-sec}^{-1}$)

The Kinetics of Complex Formation of Nickel(II)

The kinetics of complex formation of nickel(II), of all the +2 metal ions, has been most thoroughly studied (43-47). Table VI gives the various rate-constant values for the reaction of nickel(II) with various ligands. Most of these reactions are relatively fast and require temperature-jump or stop-flow techniques in order to study the reaction kinetics, so most of the rates have an error of $\pm 10\%$ to $\pm 20\%$. However, the rate constants are nearly independent of the entering ligand used. All rates are slower than the rate of solvent exchange. The same substitution reactions using methanol as the solvent proceed about one-tenth as fast as the aqueous reactions. The rate of methanol exchange is about one-tenth that of water exchange (44). These data led to postulation of the following mechanisms (38-49).



Both mechanisms are similar and involve the formation of an outer-sphere complex as a necessary intermediate. All of the available data are explained by these mechanisms. Unfortunately it has not been possible to determine K_0 experimentally. As a result K_0 must be estimated by

TABLE VI
THE RATES OF FORMATION OF SOME COMPLEXES OF NICKEL(II) AT 25° C

Temp. °C	Ligand	k_f	Solvent	Ref.
25	1,10-phenanthroline	$2.7 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(43)
25	"	$4.1 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(48)
25	"	$3.2 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(42)
25	glycine	$1.5 \times 10^4 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(45)
25	diglycine	$2.1 \times 10^4 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(45)
25	bioxalate	$5 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(47)
25	water	$3 \times 10^4 \text{sec}^{-1}$	H ₂ O	(49)
25	methanol	$1 \times 10^3 \text{sec}^{-1}$	MeOH	(44)
25	1,10-phenanthroline	$3.5 \times 10^2 \underline{M}^{-1} \text{-sec}^{-1}$	MeOH	(44)
25	bipyridine	$1.6 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	H ₂ O	(42)
25	"	$1.1 \times 10^3 \underline{M}^{-1} \text{-sec}^{-1}$	25% H ₂ O/ 75% MeOH	(44)
25	"	$8.0 \times 10^2 \underline{M}^{-1} \text{-sec}^{-1}$	3% H ₂ O/ 97% MeOH	(44)
25	"	$1.4 \times 10^2 \underline{M}^{-1} \text{-sec}^{-1}$	100% MeOH	(44)

equation I (50) which is only applicable to ion-ion interactions, or by estimating a value for the water exchange rate from other data and using equation III.

$$\text{I. } K_o = \frac{4\pi N a^3}{3000} \exp (-U(a)/kT)$$

$$\text{II. } U(a) = \frac{Z_1 Z_2 e^2}{aD} - \frac{Z_1 Z_2 e^2 u}{D(1-ua)}$$

$$\text{III. } K_o = \frac{k_{\text{obs}}}{k_{\text{water exchange}}}$$

In these equations, N is Avogadro's number, a is the distance of closest approach of the two ions (usually taken to be about 5\AA in water, 6\AA in methanol), k is Boltzmann's constant, T is the absolute temperature, e is the electronic charge, D is the solvent dielectric constant, u is the ionic strength and Z_i is the charge on ion i (42). The values obtained by this equation are probably accurate only to a factor of three or four. However, agreement between the values of k_o for several reactions involving different ligands, calculated from $k_o = \frac{k_{\text{obs}}}{K_o}$ is remarkable (44).⁷ This is in accord with the proposed mechanism, indicating that ligand participation in the transition state has a very small effect on the reaction energetics. If ligand participation is small, k_o would be equal to the rate of solvent exchange, k_{ex} , times some steric factor, f : $k_o = f k_{\text{ex}}$. This factor, f , accounts for water exchange taking place at some point in the complex, remote from the outer-sphere position of the entering ligand. Such water exchange would not give the final product which would lead to k_o values smaller than

k_{ex} . While values of K_o are open to criticism, results in water and methanol, with a wide assortment of ligands, are best explained by the outer-sphere-complex mechanism.

Platinum is in the same group of the periodic chart as nickel. In the oxidation state +2, it forms four-coordinate square planar complexes. The rate of chloride exchange in $PtCl_4^{=}$ depends mainly on the rate of aquation of the tetrachloroplatinate(II) ion (51-57). Table VII lists rate and equilibrium constants for the aquation and chloride exchange reactions of $PtCl_4^{=}$ and $PtCl_3H_2O^-$.

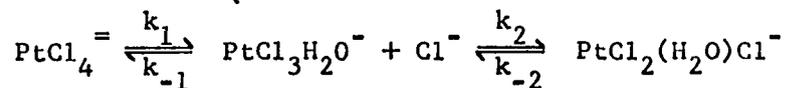
The rate constant, k_{-1} , of the following reaction was $2.8 \times 10^{-3} \underline{M}^{-1}\text{-sec}^{-1}$:



Reactions with rate constants of this magnitude are convenient systems for kinetic studies by conventional methods. They have half-lifetimes of several hours, which allows adequate time for measurement of concentrations by virtually all standard methods.

TABLE VII

SOME RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION

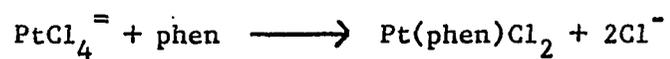


T° C	u	$K_1 = \frac{k_1}{k_{-1}}$		$10^3 K_1 (\text{M})$	$K_2 = \frac{k_2}{k_{-2}}$		Ref.
		$10^5 \times k_1 (\text{sec}^{-1})$	$10^3 \times k_{-1} (\text{M}^{-1}\text{-sec}^{-1})$		$10^5 K_2 (\text{sec}^{-1})$	$10^3 K_2$	
25	0.318	3.86	2.14	18	4.44		(51)
25	0.1	3.9	2.19				(54)
25	0.5	3.69	2.81				(56)
25	0.5	3.59		13 ± 1			(56)
25	0.318			15 ± 2		0.5 ± 0.3	(53)
25	0.1			30 ± 15		1.0 ± 0.6	(53)
25	0.05			18			(54)
10				13 ± 1			(55)

CHAPTER 2

PURPOSE

The unusual character of 1,10-phenanthroline, combined with relatively slow rates of substitution and exchange (44-51) of $\text{PtCl}_4^{=}$, led to a study of the reaction:



CHAPTER 3

EXPERIMENTAL

K₂PtCl₄

Potassium tetrachloroplatinate was prepared by the reduction of K₂PtCl₆, as originally suggested by Vezes (52). The K₂PtCl₆ was prepared by treating platinum metal with aqua regia followed by repeated evaporations with hydrochloric acid. The K₂PtCl₆ was precipitated by the addition of potassium carbonate and potassium chloride.

Pt(phen)Cl₂

Dichloro(1,10-phenanthroline)platinum(II) was prepared under exactly the same conditions as the kinetics experiments described in the following section. Four-hundred and fifteen mg K₂PtCl₄ were added to one liter of a solution containing 190 mg 1,10-phenanthroline, 580 mg NaCl, and 0.85 ml concentrated HCl. The mixture was warmed to 45° C and allowed to stand for several days. The dichloro(1,10-phenanthroline)platinum(II) was removed from the solution by vacuum filtration and dried overnight in a vacuum desiccator. Yield, based on the weight of K₂PtCl₄ used, 460 mg (99%). Anal. Calc. for Pt(C₁₂H₈N₂)Cl₂ : Pt, 43.72; C, 32.27; H, 1.779; Cl, 19.89. Found: Pt, 43.90; C, 32.22; H, 1.85; Cl, 15.93.

All other chemicals were reagent grade. Conductivity measurements were made on an Industrial Instruments model RC-16B2 conductance bridge.

Rates of Substitution Reactions

The rates of substitution of $\text{PtCl}_4^=$ by 1,10-phenanthroline were determined over a range of concentrations of both reactants of $5 \times 10^{-4}\text{M}$ to 10^{-3}M . The procedure described is typical of all reactions.

One-hundred ml solution was prepared containing $1 \times 10^{-3}\text{M}$ 1,10-phenanthroline (1×10^{-4} moles), $1 \times 10^{-2}\text{M}$ sodium chloride, $1 \times 10^{-2}\text{M}$ HCl, and enough NaBF_4 to give the desired ionic strength. The solution was thermostated at $55^\circ \text{C} \pm 0.02^\circ \text{C}$ for about two hours, or until thermal equilibrium had been reached. The solution was poured rapidly into a four-ounce bottle containing 41.5 mg (1×10^{-4} mole) K_2PtCl_4 . This was shaken vigorously to dissolve the very soluble K_2PtCl_4 and placed in the constant temperature bath.

Samples of 5 ml each were drawn at regular intervals and pipetted into 15 ml of 0.05M ferrous ammonium sulfate solution. Iron(II) reacted very rapidly and quantitatively with 1,10-phenanthroline to form an intensely-colored water soluble complex (25). The solutions were filtered after 1000 seconds. The absorption maxima of the iron-phenanthroline complex at 5100 Angstroms were measured after about 2500 seconds using a Beckman DU spectrophotometer. The concentration of 1,10-phenanthroline at the time of sampling was considered to be the same as the concentration of the iron-phenanthroline complex and was determined by comparison of the observed absorption with a previously prepared plot of known concentrations versus absorption. In pure water, a straight line plot was obtained using a second-order rate equation, first-order in phenanthroline, and first-order in K_2PtCl_4 .

Because most phenanthrolines are only slightly soluble in water, it was decided to study the reaction in both water and in a mixed solvent of 50% ethanol, 50% water. In mixed solvent systems such as ethanol-water, acetone-water, diglyme-water, and methanol-water, a straight line fit was obtained by plotting concentration of 1,10-phenanthroline versus time, a zero-order plot. Typical reaction data are shown in Table XII (see page 65), plots of this data in Figures 12 and 14 (see pages 47 and 50).

In order to measure the kinetic isotope effect without the use of large quantities of solvent, it was necessary to use 4,7-diphenyl-1,10-phenanthroline-X,X-disulfonate, which gave a soluble product, in place of the 1,10-phenanthroline. The rate of reaction was measured at 254 μ , using a Beckman DU spectrophotometer. The solvent was 50% aqueous ethanol, either deuterated or non-deuterated.

Equilibrium Constants and Rates of Aquation of K_2PtCl_4

The equilibrium constant and rates of aquation of K_2PtCl_4 were determined using the method of Grantham, Elleman, and Martin (51). Potassium tetrachloroplatinate, 83.0 mg (2×10^{-4} moles), NaCl, 107 mg (2×10^{-3} moles), and enough $NaClO_4$ to give an ionic strength of 0.1 were added to water to make 100 ml of solution. The solution was aged for 48 hours at $45 \pm 0.05^\circ$ C and was then titrated with 0.010 M NaOH over a period of about 20 minutes to determine the titration curve. Another solution was prepared and titrated to the end point of the original solution. The result showed an error of about 2%, probably

due to additional aquation of the original solution as it was titrated. The concentration of $\text{PtCl}_3\text{H}_2\text{O}^-$ was calculated from the equivalents of base. Using this value plus the original concentrations, the equilibrium constant was calculated to be 2.52×10^{-2} moles-liter⁻¹ at 45° C. Similar titrations at 65° C yielded a value of K equal to 2.8×10^{-2} moles-liter⁻¹.

The rate of aquation of $\text{PtCl}_4^{=}$ in solution was found by preparing a solution of 2×10^{-3} molar K_2PtCl_4 at 45° C. At regular intervals aliquots were withdrawn from the solution, and enough NaOH solution was added quickly to neutralize about 50% of the $\text{PtCl}_3\text{H}_2\text{O}^-$ present. The time of sampling and pH of the resulting solution were recorded. The actual percent neutralization of the solution was taken from a previously prepared, corrected titration curve. The concentration of $\text{PtCl}_3\text{H}_2\text{O}^-$ at the time of titration was calculated using the equivalents of base and percent neutralization. From this datum and the equilibrium constant, the rate constants at 45° C were computed to be $k_1 = 1.5 \times 10^{-3} \text{ sec}^{-1}$ and $k_{-1} = 5.95 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$.

The Rate of Decomposition of K_2PtCl_4 in 50% Ethanol

Two-hundred ml of a 50% ethanol solution was prepared and thermostated at $45 \pm 0.1^\circ$ C in a stirred, jacketed beaker. Forty-one and five-tenths mg K_2PtCl_4 was added to the solution. The conductivity of the solution was measured at regular intervals and recorded along with the time of measurement. After several hundred seconds a black precipitate was observed, whereupon the rate of change of the conductance accelerated until all of the K_2PtCl_4 had decomposed.

CHAPTER 4

RESULTS

The Substitution Reaction of K_2PtCl_4
by 1,10-Phenanthroline in Water

When K_2PtCl_4 and 1,10-phenanthroline were dissolved in water, they reacted slowly to give $Pt(phen)Cl_2$. After a short induction period, the reaction proceeded to completion by a second-order path.

Figure 12 shows a typical graph of the second-order reaction. The second-order rate constants for the reaction under various conditions of concentration and temperature are shown in Table VIII.

TABLE VIII

SECOND-ORDER RATE CONSTANTS OF THE REACTION BETWEEN K_2PtCl_4 AND
1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS AND AT A pH
OF 2.0 AND IONIC STRENGTH OF 2.3×10^{-2}

$t^\circ C$	$10^3 [PtCl_4^{2-}] (M)$	$10^3 [phen] (M)$	$10^2 [Cl^-] (M)$	$10^3 k_2 (M^{-1} \text{-sec}^{-1})$
45	0.50	0.50	2.2	4.5 ± 0.0
55	1.00	1.00	2.0	11.4 ± 0.3
55	0.50	1.00	2.0	11.5 ± 0.3
55	1.00	0.50	2.0	11.9 ± 0.9
55	1.50	1.00	2.0	11.4 ± 0.1
55	1.00	1.50	2.0	11.4 ± 0.0
55	1.00	1.00	2.2	11.2 ± 0.0
65	1.00	1.00	2.2	24.6 ± 0.0
65	1.00	1.00	2.0	24.4 ± 0.1

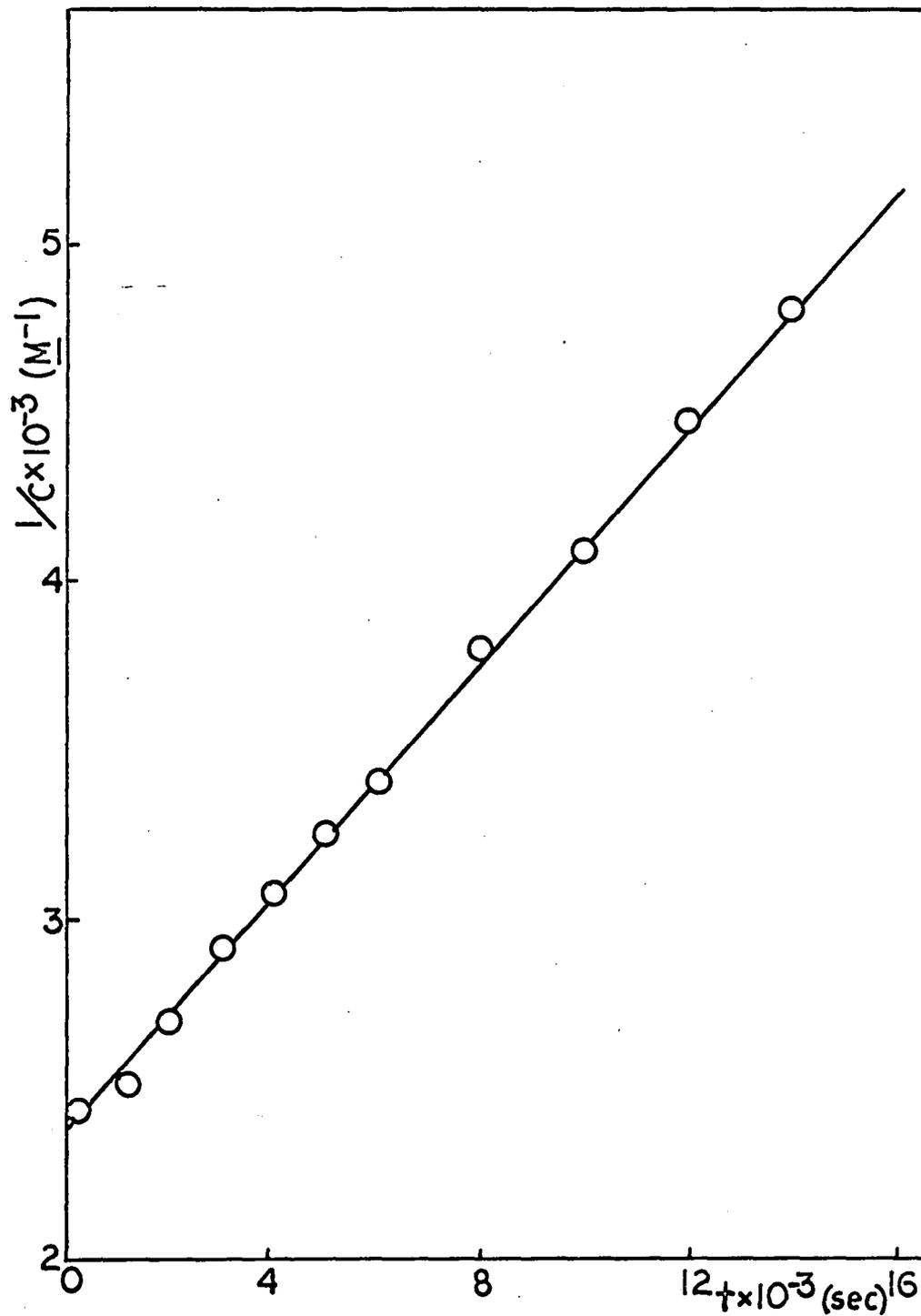


Figure 12. The Rate of Disappearance of 1,10-Phenanthroline Versus Time at 55° C

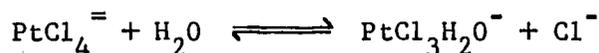
The initial concentration of $[\text{PtCl}_4^{=}] = [\text{phen}] = 1.0 \times 10^{-3} \text{ M}$;
 $[\text{Cl}^-] = 2.0 \times 10^{-2} \text{ M}$; pH = 2.0; ionic strength = 2.3×10^{-2} .

The Rate Dependence on Changing
Chloride Ion Concentration

An increase in chloride ion concentration at constant ionic strength caused a decrease in the rate of the reaction. The relationship was not a simple one but gave rise to an S-shaped curve when $\log k$ versus $[\text{Cl}^-]$ was plotted (Figure 13).

The Aquation Reaction of $\text{PtCl}_4^{=}$

According to the following reaction the reversible aquation of $\text{PtCl}_4^{=}$ might offer a path for phenanthroline substitution:



Since the equilibrium and rate constants for the reaction were not available at 45° C to 65° C, some experimental values were determined at 55° and 65° C so that the importance of this process in the substitution reaction could be evaluated. The equilibrium constants were: $K_o = 2.52 \times 10^2 \text{ M}^{-1}$ at 55° C and $2.8 \times 10^{-2} \text{ M}^{-1}$ at 65° C. The rate constant for the aquation reaction was $1.5 \times 10^{-3} \text{ sec}^{-1}$ at 55° C. The half-life of the reaction was 460 seconds.

The Effect of Changing Ionic Strength

An increase in ionic strength at constant reactant and chloride ion concentrations caused a decrease in the rate of the reaction (Figure 14). The relationship was the expected one and the calculated charge product of the reactants was -1.96. This is indicative of, but definitely not proof for, a doubly-charged, negative ion playing an important role in the rate-step. However, at the concentrations involved,

Figure 13. The Rate of Formation of Pt(phen)Cl₂ in Water Versus log [Cl⁻] at 55° C

The initial concentration of [PtCl₄⁻] = [phen] = 1.0 x 10⁻³ M;
pH = 3.0; ionic strength = 10.3.

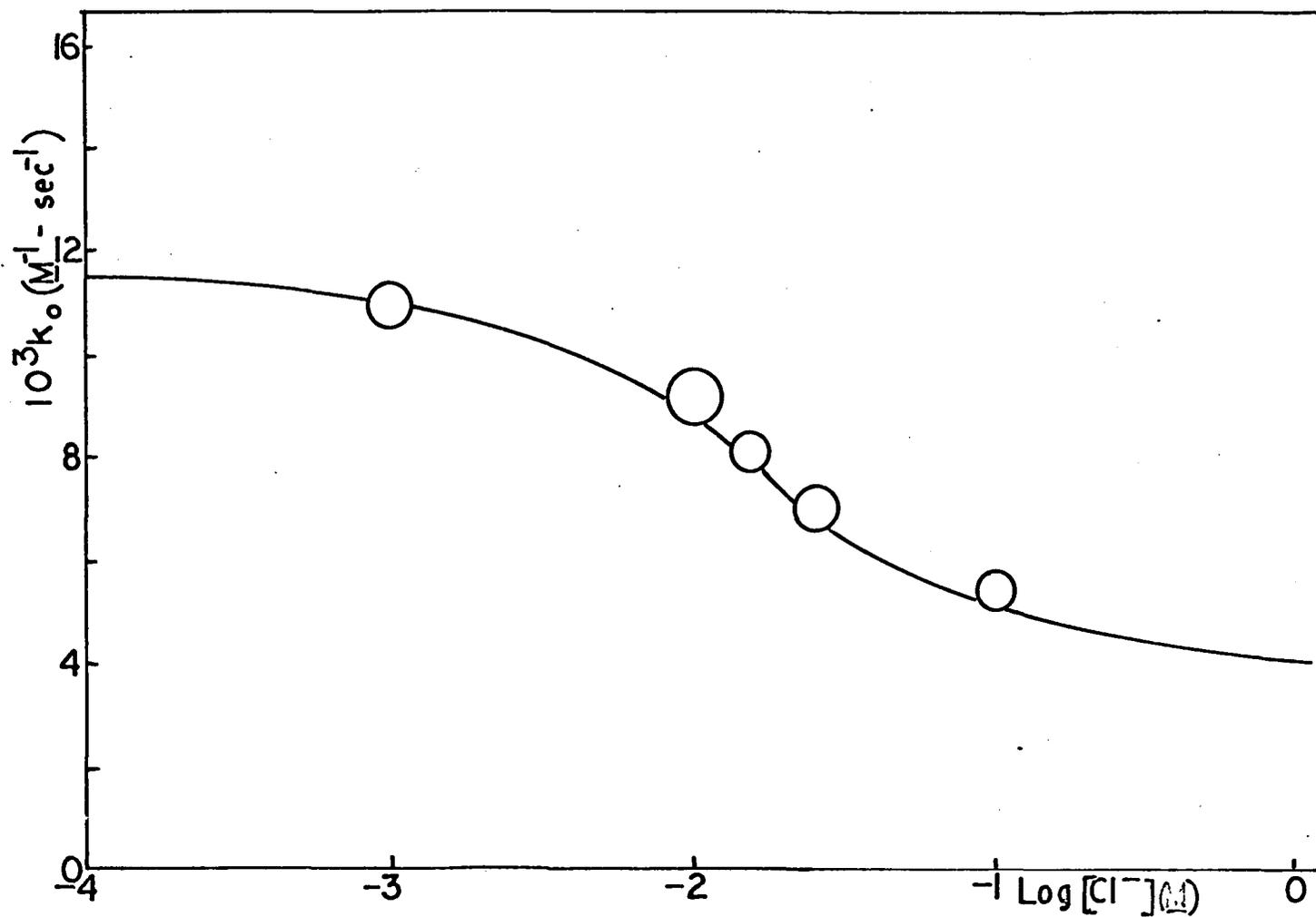


Figure 13. The Rate of Formation of $Pt(phen)Cl_2$ in Water Versus $\log [Cl^-]$ at $55^\circ C$

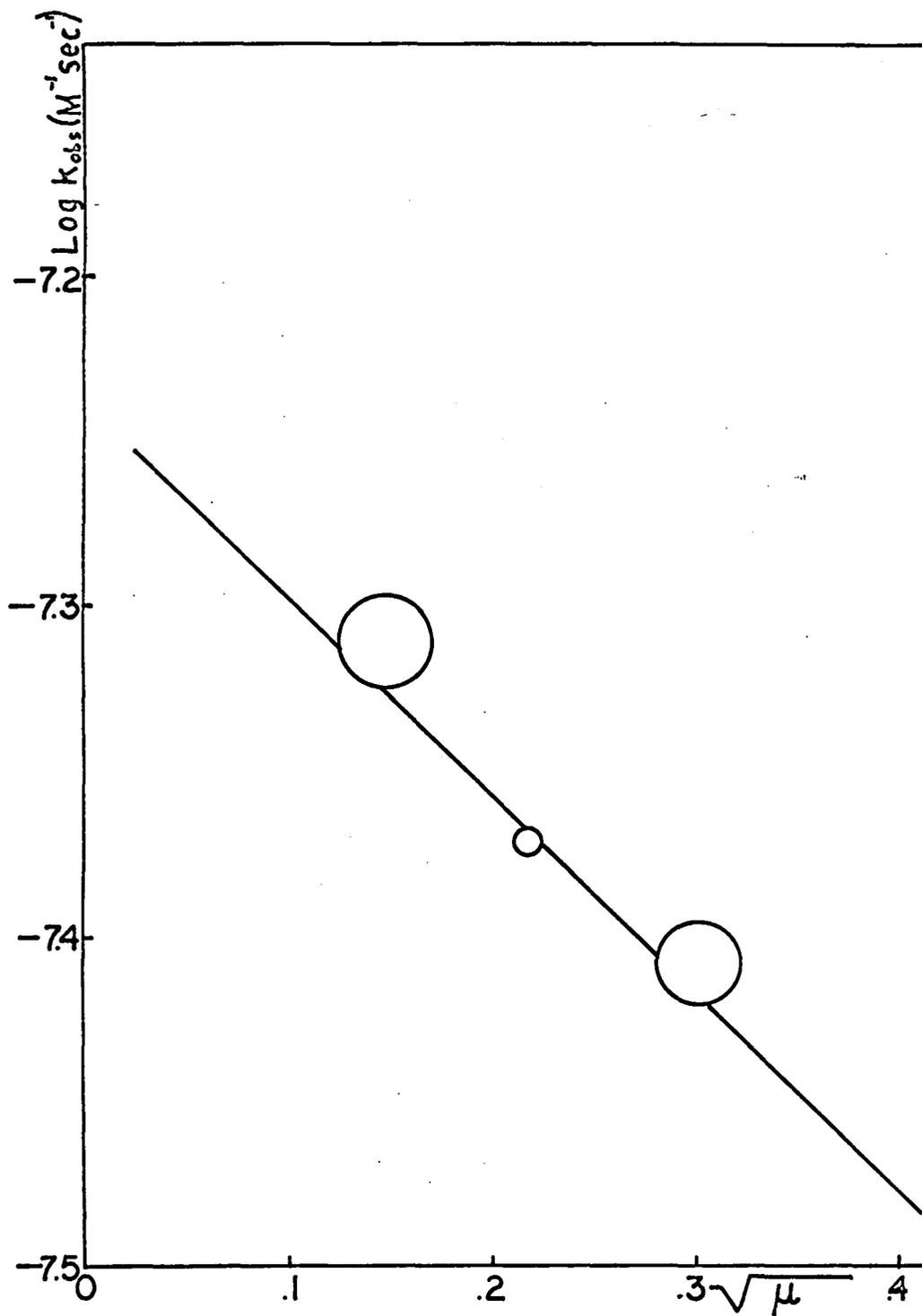


Figure 14. The Rate of Formation of $\text{Pt}(\text{phen})\text{Cl}_2$ in Water Versus the Square Root of Ionic Strength at 55°C .

The initial concentration of $[\text{PtCl}_4^{2-}] = [\text{phen}] = 1.0 \times 10^{-3} \text{M}$;
 $[\text{Cl}^-] = 1.0 \times 10^{-3} \text{M}$; $\text{pH} = 3.0$.

the applicability of this relationship is questionable. These results certainly do not rule out the possibility of a singly-charged ion playing an important role in the rate-determining steps of the mechanism.

TABLE IX

SOME SECOND-ORDER REACTION RATE CONSTANTS FOR THE REACTION BETWEEN VARIOUS Pt CONTAINING COMPLEXES AND LIGANDS

T° C	Complex	Ligand	$k_2 (\text{M}^{-1} \text{sec}^{-1})$
45	$\text{PtCl}_4^{=}$	1,10-phenanthroline	0.0045
		4,7-dimethyl-1,10-phenanthroline	0.0059
		5,6-dimethyl-1,10-phenanthroline	0.0020
		2,2-bipyridyl	0.012
25		ethylenediamine	0.094
45	$\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$	1,10-phenanthroline	4.0
65	$\text{cis-Pt}(\text{NH}_3)_2(\text{Cl})_2$		0.00012
65	$\text{trans-Pt}(\text{NH}_3)_2(\text{Cl})_2$		< 0.00001

The Effect of Changing pH

Variation of pH over a range of 2.3 to 4.9 produced only a slight change in the rate of reaction. In this pH range aquo complexes of platinum do not dissociate to give hydroxo complexes. There is a large change in the relative amounts of phenanthroline and phenanthroline ion.

The Effect of Other Ligands on the Rate
of the Substitution Reaction

Since the rate of reaction was dependent on the phenanthroline concentration, the nucleophilicity dependence was investigated by using substituted phenanthroline in place of the 1,10-phenanthroline. The 5,6-dimethyl and 4,7-dimethyl derivatives of 1,10-phenanthroline were used. The 5,6-dimethyl derivative is about 0.2 times as basic as 1,10-phenanthroline; the 4,7-dimethyl is ten times more basic (58). It was assumed that a change in nucleophilicity would be reflected by a change in basicity. The methyl groups were assumed to be far enough removed from the coordination sites to render steric effects negligible. The data in Table IX show that there was a rate increase with increased basicity or nucleophilicity of the phenanthroline.

An attempt was made to determine which of the chlorides were being replaced by substituting amino groups for two of the chlorides in both the cis- and trans- positions. The compounds cis-PtCl₂(NH₃)₂ reacted about 10,000 times slower than the PtCl₄⁼; the trans- complex did not seem to react at all (Table IX). Only a small sample of the product of reaction between 1,10-phenanthroline and cis-Pt(NH₃)₂Cl₂ was isolated. The results were so inconclusive that this line of investigation was dropped.

The Reaction of PtCl₄⁼ with 1,10-Phenanthroline
in Mixed Solvents

When 1,10-phenanthroline, dissolved in ethanol, was mixed with K₂PtCl₄ in water, they reacted to form Pt(phen)Cl₂ at a rate expressed by $\frac{d(\text{phen})}{dt} = k_o$. As in water, the reaction went to completion and no

induction period was observed. If $\text{PtCl}_4^=$ was in excess, a precipitate of platinum metal formed slightly before all of the phenanthroline was gone. A short induction period occurred in reactions in which solid K_2PtCl_4 was added to a mixed solvent containing the phenanthroline. Figure 15 is a sample graph of such a reaction.

The observed rate constants and conditions of the reactions are listed in Table X. Plots of $[\text{PtCl}_4^=]_{\text{initial}}$ versus k_{obs} and $[\text{ethanol}]$ versus k_{obs} (Figures 16 and 17) show first-order rate dependences. Because of the large excesses of ethanol employed in the reaction, the ethanol concentration would be nearly constant over the course of the reaction. This would lead to the rate dependence that was observed, even if ethanol underwent a chemical change.

The first-order dependence of the reaction on the initial concentration of K_2PtCl_4 was neither the usual nor the expected behavior. The reaction could be followed over about an 80% change in the $\text{PtCl}_4^=$ concentration. No first-order dependence was observed as the platinum concentration decreased; therefore, the reaction was first-order only in the initial concentration of the platinum complex.

As shown in Table XII the rate of reaction was independent of the concentration of the entering ligand. In addition, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, and 5,6-dimethyl-1,10-phenanthroline gave rate constants which were identical within experimental error. This indicates an independence of the basicity and nucleophilicity for the reaction. Since the reaction rate was independent of the concentration, it is not surprising that it is also not

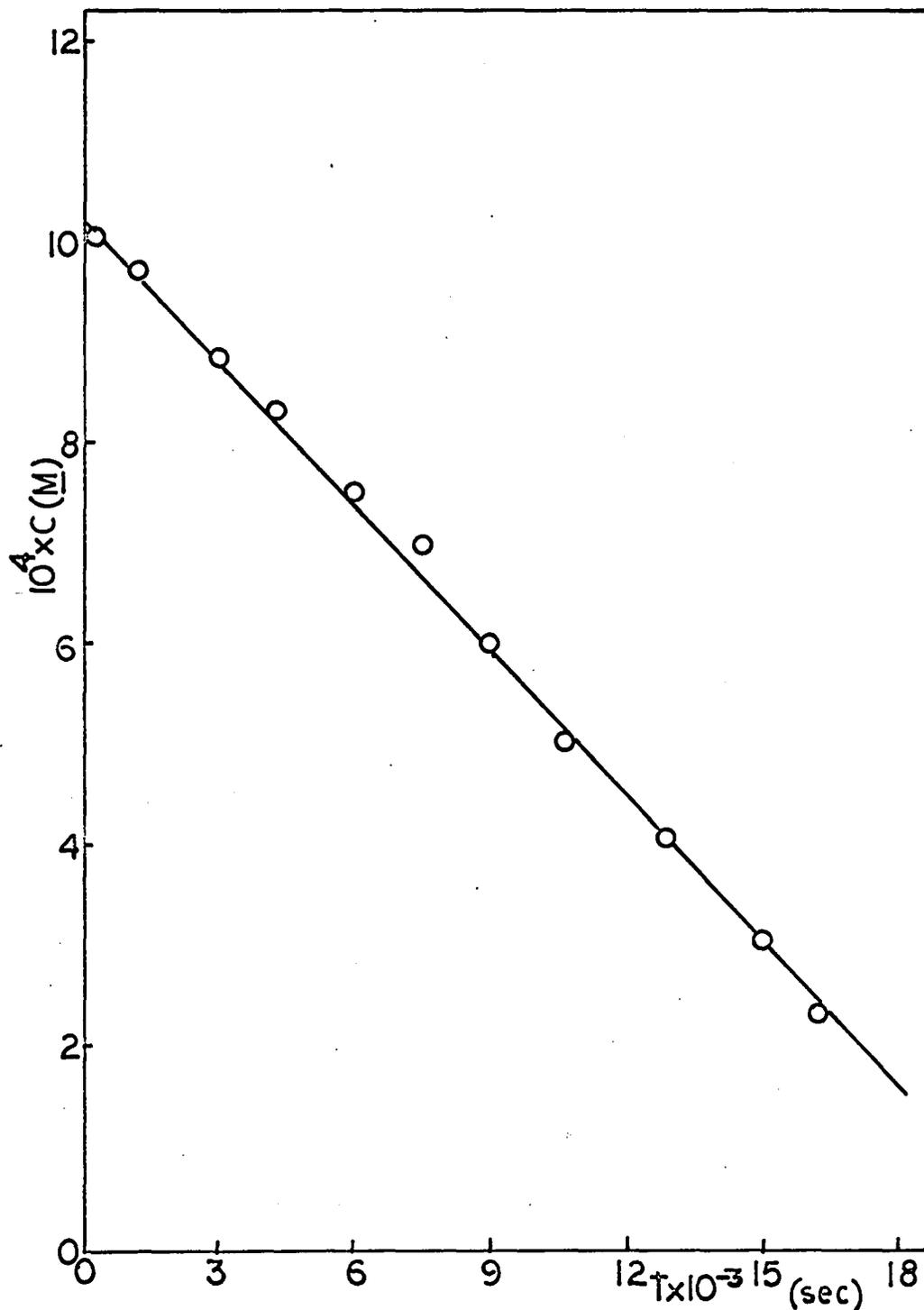


Figure 15. The Rate of Disappearance of 1,10-Phenanthroline in 50% Ethanol Versus Time at 55° C

The initial concentration of $[\text{PtCl}_4^{=}] = [\text{phen}] = 1.0 \times 10^{-3} \underline{\text{M}}$;
 $[\text{Cl}^-] = 2.0 \times 10^{-2} \underline{\text{M}}$; pH = 2.0; ionic strength = 2.3×10^{-2} .

TABLE X

SOME RATE CONSTANTS FOR THE REACTION BETWEEN K_2PtCl_4 AND
1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS

$T^\circ C$	%EtOH	$[Pt] \times 10^4$	$[phen] \times 10^4$	$[Cl^-] \times 10^2$	$[H^+] \times 10^2$	$u \times 10^2$	$k_o \times 10^8 (M/sec)$
45	25	10.0	5.0	2.00	2.0	2.3	2.04 ± 0.01
	37.5	10.0	5.0	2.00	2.0	2.3	3.60 ± 0.01
	50	10.0	5.0	2.00	2.0	2.3	4.88 ± 0.13
	75	10.0	5.0	2.00	2.0	2.3	6.20 ± 0.01
	50	2.5	5.0	2.00	2.0	2.3	1.11 ± 0.01
	50	5.0	5.0	2.00	2.0	2.3	2.36 ± 0.01
	50	7.5	5.0	2.00	2.0	2.3	3.58 ± 0.01
	50	10.0	10.0	2.00	2.0	2.3	4.79 ± 0.04
	50	5.0	5,6-DMP	2.3	2.0	2.6	2.15 ± 0.14
	50	5.0	4,7-DMP	2.3	2.0	2.6	2.14 ± 0.04
	50	5.0	5.0	5.0	2.0	5.3	1.80 ± 0.01
	50	5.0	5.0	10.0	2.0	10.3	1.10 ± 0.01
	50	10.0	10.0	0.1	2.0	10.3	5.85 ± 0.07

TABLE X--Continued

T° C	%EtOH	[Pt]x10 ⁴	[phen]x10 ⁴	[Cl ⁻]x10 ²	[H ⁺]x10 ²	ux10 ²	k _o x10 ⁸ (M/sec)	
	50	10.0	10.0	1.0	2.0	10.3	4.80	0.14
	50	10.0	10.0	2.0	2.0	10.3	3.80	0.14
	50	10.0	10.0	5.0	2.0	10.3	2.65	0.07
	50	10.0	10.0	10.0	2.0	10.3	2.25	0.10
	50	5.0	5.0	2.3	2.0	2.6	2.05	0.11
	50	5.0	5.0	2.3	0.1	2.6	2.11	0.04
	50	5.0	5.0	2.3	0.025	2.6	2.33	0.06
	50	5.0	5.0	2.3	0.012	2.6	2.24	0.04
	50	10.0	10.0	2.0	2.0	5.3	4.25	0.02
	50	10.0	10.0	2.0	2.0	10.3	3.70	0.14
55	50	5.0	4,7-DMP	2.0	2.0	2.3	14.3	0.1

Figure 16. The Rate of Formation of Pt(phen)Cl_2 in 50% Ethanol Versus the Initial Concentration of PtCl_4 at 55°C

The initial concentration of phen = $1.0 \times 10^{-3} \text{M}$;
 $[\text{Cl}^-] = 2.0 \times 10^{-2} \text{M}$; pH = 2.0; ionic strength =
 2.3×10^{-2} .

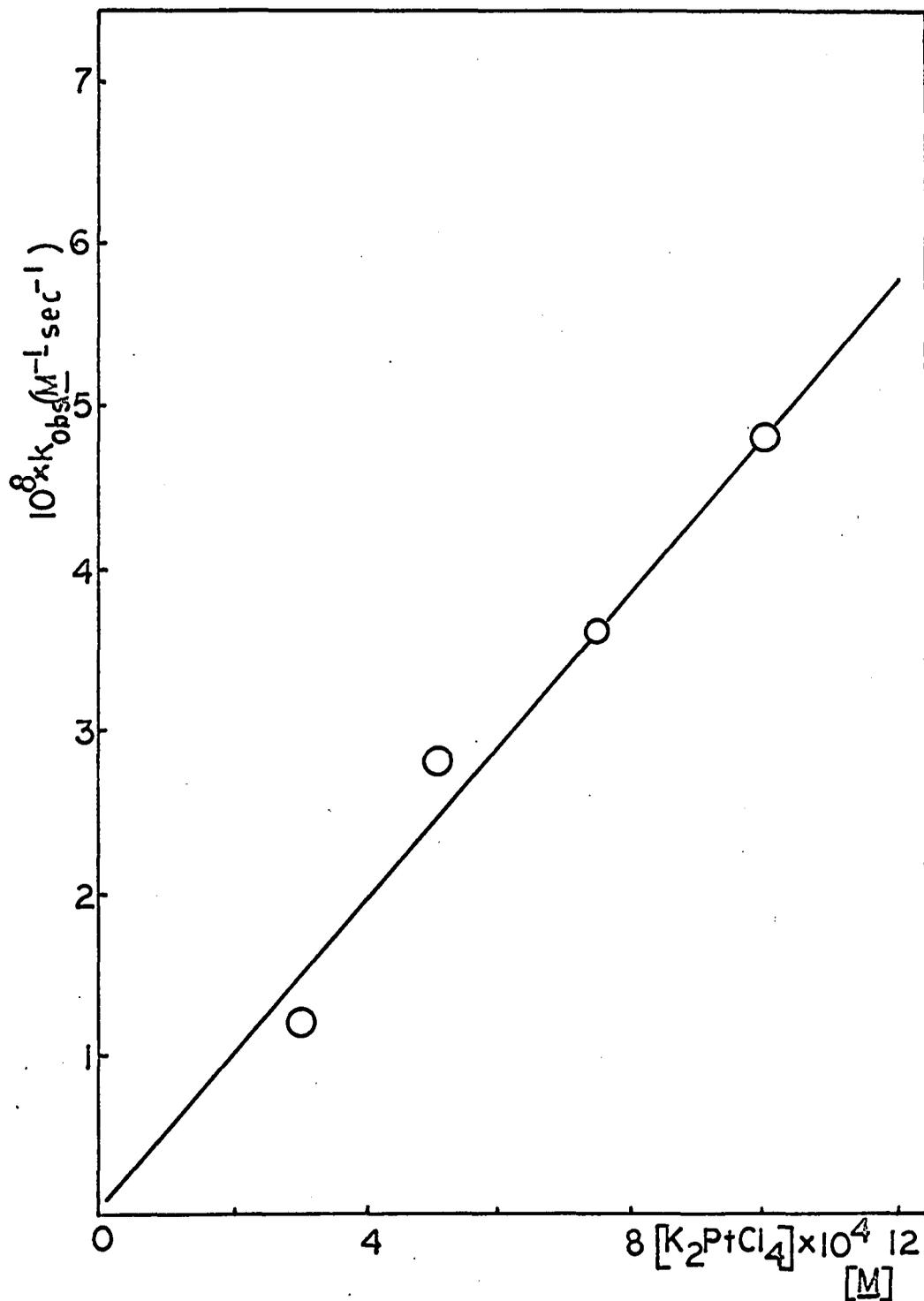


Figure 16. The Rate of Formation of $\text{Pt}(\text{phen})\text{Cl}_2$ in 50% Ethanol Versus the Initial Concentration of PtCl_4^- at 55°C

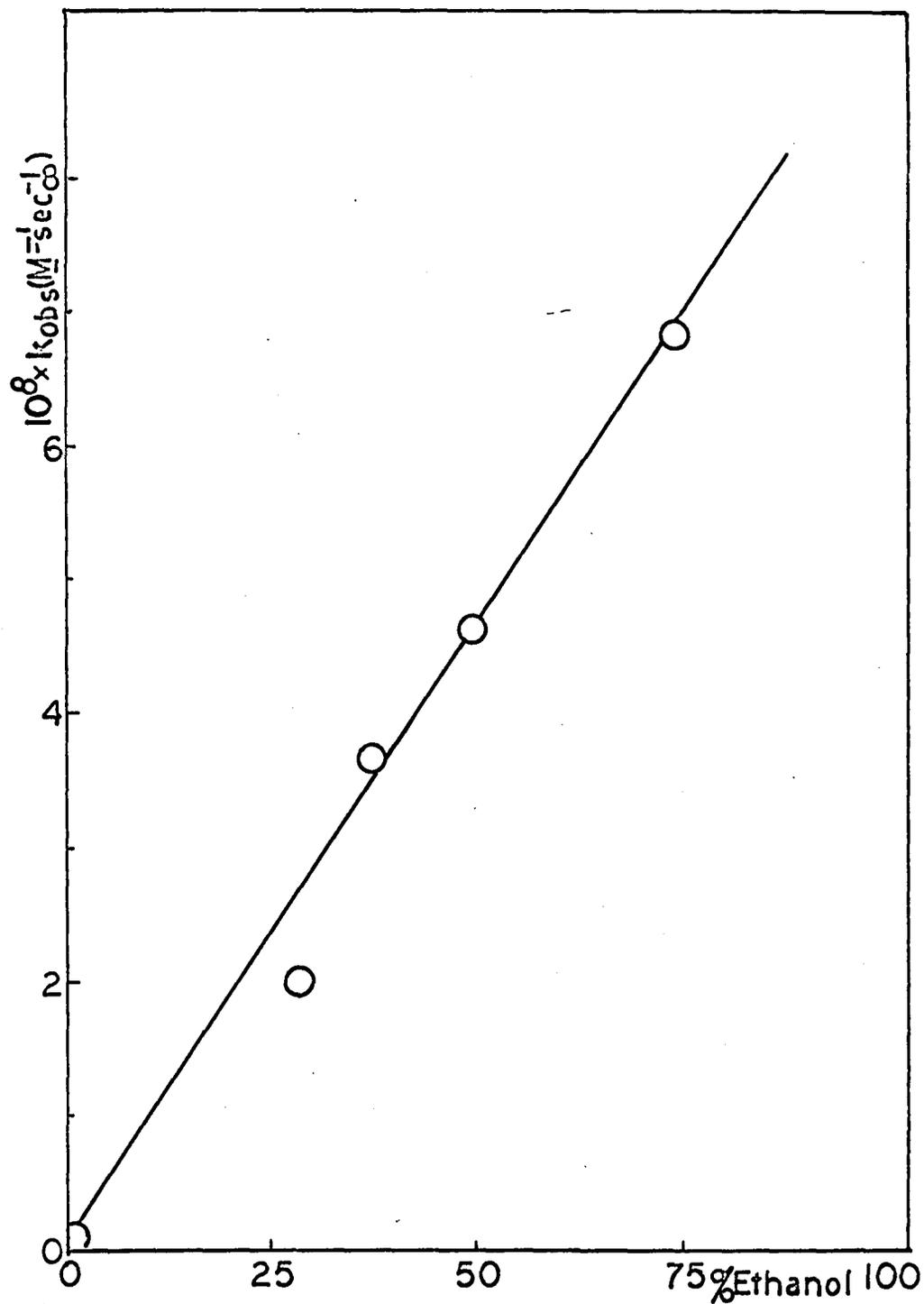


Figure 17. The Rate of Formation of Pt(phen)Cl_2 Versus % Ethanol at 55°C

The initial concentration of $\text{PtCl}_4^{2-} = [\text{phen}] = 1.0 \times 10^{-3} \text{M}$;
 $[\text{Cl}^-] = 2.0 \times 10^{-2} \text{M}$; $\text{pH} = 2.0$; ionic strength $= 2.3 \times 10^{-2}$.

affected by changes in the ligand. These results are not the same as results obtained in the aqueous reaction and cannot be explained by a simple change in dielectric constant.

As in the aquo reaction, the rate was insensitive to variation of pH over a range of 1.7 to 3.9. Since the rate was independent of the concentration of phenanthroline, there was no reason to expect a change in the phenanthroline-phenanthroline ion ratio to affect the rate of the reaction and in this pH range aquo-platinum complexes do not dissociate to form hydroxo complexes. An increase in ionic strength did produce a decrease in the rate. Although charge products tend to be rather unreliable at the concentrations involved, the charge product was only -0.35 , a much smaller value than the -1.96 obtained in water. This value indicates that some neutral molecule was taking an important part in the rate step of the reaction. Since phenanthroline did not appear in the rate equation, it cannot be the neutral molecule that gave rise to this charge product. The solvent, whether water or ethanol, might be such a molecule.

The reaction showed a kinetic isotope effect. The ratio of k_o/kH was 2.2 ± 0.1 using 1:1 D_2O and D_6 ethanol. No effect was observed using 1:1 D_2O and H_6 ethanol. This was indicative of a secondary isotope effect dependent on the breaking of a platinum to ethanol-oxygen bond (59) being part of some rate-determining step.

The Solvolysis of K_2PtCl_4 in 50% Ethanol

Since isotope effects and chloride ion dependence indicated that some rate-determining reaction probably involved the platinum complex

and ethanol, an attempt was made to study the solvolysis of $\text{PtCl}_4^=$ by ethanol in a 50% ethanol solution.

If all glassware was very clean, there was a small, steady increase in free chloride for several hundred seconds, then a very rapid formation of metallic platinum. This second phase usually took about 100 seconds to reduce more than 99% of the platinum. The initial rate seemed to be about as fast as the zero-order reaction with phenanthroline. However, because of the short time that the reaction could be observed, relative to $t_{\frac{1}{2}}$, it was not possible to determine the kinetic order of this solvolysis reaction. Any small amount of metallic platinum formed seemed to immediately initiate the second phase of the reaction.

Dependence of the Rate on Chloride Ion Concentration

An increase in chloride ion concentration at constant ionic strength caused a decrease in the reaction rate. As in water, the relationship was not a simple linear one, but S-shaped. Again, some solvated species and the unsolvated $\text{PtCl}_4^=$ are probably involved, but because of the complexity of the possible intermediates, no attempt was made to isolate the rate constants.

The Reaction Between K_2PtCl_4 and 1,10-Phenanthroline in the Presence of Possible Catalysts

Since the reaction seemed to be catalyzed by the ethanol, or an impurity in the ethanol, an attempt was made to study the effect of various agents which could have been present in the ethanol or which

could have been formed by some reaction between ethanol and the PtCl_4^- . These results are listed in Table XI.

Hydride Ion

Upon reaction with certain transition metal complexes, ethanol is known to produce hydride ion (60). This hydride acts as a strongly labilizing ligand catalyzing a further reaction. Hydride ion, as an aliquot of sodium borohydride solution, was added to aqueous reactions after all of the reactants, except the acid, had been added. The acid was added after several minutes, allowing the hydride ion to react with the platinum complex. At concentrations of hydride ion about equal to the reactant concentration, the rate of reaction was increased:

$$k_2 = 6.7 \times 10^{-2} \text{ M}^{-1} \text{-sec}^{-1} \text{ versus } 4.5 \times 10^{-3} \text{ M}^{-1} \text{-sec}^{-1} \text{ in water}$$

However, at higher concentrations of hydride ion all platinum was reduced to the metal. It is clear that the hydride ion can catalyze the reaction but this does not account for the change in mechanism nor for the strange behavior of the rate with PtCl_4^- .

Ethylene

It has been shown that Zeise's salt, $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$, reacts very rapidly with phenanthroline to produce $\text{Pt}(\text{phen})\text{Cl}_2$ (Table XI).

Under appropriate conditions, ethanol also may be dehydrated to give ethylene: $\text{vis } \text{CH}_3\text{-CH}_2\text{-OH} \xrightarrow{\text{cat.}} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$.

A mixture of about 90% K_2PtCl_4 and 10% $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3$ was used as a source of ethylene in solution. The rate was only slightly faster

TABLE XI

THE CATALYTIC EFFECT OF VARIOUS MATERIALS ON THE REACTION
OF K_2PtCl_4 WITH 1,10-PHENANTHROLINE

$[PtCl_4^{2-}] = [phen] = 5 \times 10^{-4} M; u = 2.3 \times 10^{-2}; T = 45^\circ C, pH = 2.0$					
Catalyst	Conc.	k_{obs}	Rate Order	$t_{1/2}$ (sec)	$t_{1/2}^{EtOH}/t_{1/2}^{cat.}$
none	0	4.5×10^{-3}	2	44.5	0.023
EtOH	50%	2.4×10^{-8}	0	1.04	1
C_2H_4	$5 \times 10^{-5} M$	5.0×10^{-3}	2	40	0.025
C_2H_4	$2 \times 10^{-3} M$	5.6×10^{-4}	1	.123	8.45
H^-	$1 \times 10^{-4} M$	5.4×10^{-3}	2	37	0.0281
H^-	$2 \times 10^{-4} M$	6.7×10^{-3}	2	29.8	0.035
Pt metal	?	4.5×10^{-3}	2	44.5	0.023
$Pt^0 [P(OEt)_3]_4^a$	$0.03 \times 10^{-5} M$	4.5×10^{-3}	2	44.5	0.023
$Pt^0 [P(OEt)_3]_4^b$	$1.3 \times 10^{-5} M$	5.4×10^{-3}	2	37	0.028

a. Introduced as an ethanolic solution

b. Introduced as a solution in diglyme

than the normal aqueous reaction. Low concentrations of ethylene, about $5 \times 10^{-5} \text{M}$, were used with the same results. A ten-fold excess of ethylene to $\text{PtCl}_4^{=}$ gave an observed, relatively fast, first-order reaction. The equilibrium between ethanol and ethylene was calculated from heats of formation and solution. Consequently, the amount of ethylene formed would be too small to account for the observed results.

Platinum Metal

Small amounts of heterogeneous catalysts sometimes produce zero-order kinetic rates. Platinum metal was the only likely heterogeneous catalyst, because the vessels used in all experiments were the same and no catalysis was noted in the absence of ethanol. When a small amount of platinum metal was generated in the reaction flask and the 1,10-phenanthroline added, the reaction rate was identical with the rate observed in pure water.

Platinum(0)

The equilibrium between platinum(0), platinum(II), and platinum(IV) (61) has been established. Since platinum(0) would be formed in the reaction mixture, it was studied as a possible catalyst. Here the mechanism would be similar to the one suggested for the labilization of platinum(IV) complexes by platinum(II) or rhodium(II) by rhodium(I) (60).

Platinum(0) was furnished by Dr. Fred Basolo as the compound $\text{Pt}[\text{P}(\text{OEt})_3]_4$. This compound was easily oxidized and very labile. The compound was added to a prepared reaction mixture as a solution in

either oxygen-free ethanol or diglyme. The small increase in rate observed in the diglyme solution might be due to some slight catalytic effect of the platinum(0) or to effects caused by the diglyme or triethyl phosphite impurities.

Mixed Solvents Other Than Ethanol-Water

In an effort to gather more information about the possible catalytic specie present in the reaction of K_2PtCl_4 with 1,10-phenanthroline in 50% ethanol, a brief study of other mixed solvent systems was undertaken. Table XII shows the rate constants for the reactions under various solvent conditions. All solvent systems studied gave zero-order kinetic rates.

Methanol-water was first used as a solvent system because it was most unlikely that ethylene would be produced by some reaction between methanol and platinum. Therefore, if ethylene were the catalyst, the reaction should have proceeded at a rate comparable to the rate in pure water and, by similar mechanism, give second-order kinetic results. The reaction was again pseudo-zero-order with a rate dependent on the methanol concentration. No investigation was made of the $[PtCl_4^{=}]$ dependence.

If one assumed that the formation of a solvent complex was somehow involved in the rate step(s) of the reaction, then the difference in rates of the reaction in ethanol and in methanol seems reasonable. Ethanol forms weaker bonds than methanol and is less nucleophilic. In fact, a reasonable ordering of the solvents used, in terms of

TABLE XII

THE OBSERVED RATE CONSTANTS FOR THE ZERO-ORDER REACTION OF K_2PtCl_4
WITH 1,10-PHENANTHROLINE IN MIXED SOLVENT SYSTEMS

Solvent	Wt. %	C	$10^8 k_{obs}$
water	100	78	0.1 ^a
acetone	50	51.2	0.95
methanol	50	57.1	1.95
dioxane	50	34.3	3.45
ethanol	50	49.4	4.85
diglyme	50	40	4.2

T = 45° C $[PtCl_4^{2-}] = [phen] = 1 \times 10^{-3} M$

a. Initial points only

nucleophilicity (62), would be: water > acetone > methanol > dioxane > ethanol \approx diglyme. Table XII shows such an ordering in the observed rate constants.

When K_2PtCl_4 was dissolved in an acidic diglyme solution, without phenanthroline, no precipitate was observed. If aliquots were withdrawn and allowed to react with a solution containing phenanthroline for a short time before quenching with iron(II) solution, reaction proceeded at a slightly slower rate than a reaction run in the usual manner. A longer induction period was observed and the reaction rate dropped to zero before all of the platinum was used. The curved line in Figure 18 is a plot of such an experiment, while the straight line is a reaction run under identical conditions except that phenanthroline and platinum complexes were present in the same solution.

Figure 18. The Rate of Disappearance of 1,10-Phenanthroline Versus Time at 45° C in 50% Diglyme

The initial concentration of $\text{PtCl}_4^{=}$ = $[\text{phen}] = 5.0 \times 10^{-4} \text{M}$; $[\text{Cl}^-] = 2.0 \times 10^{-2} \text{M}$; $\text{pH} = 2.0$; ionic strength = 2.3×10^{-1} . The solid black circles indicate the $\text{PtCl}_4^{=}$ was allowed to react with the solvent, then added to a phenanthroline solution. The open circles indicate that the $\text{PtCl}_4^{=}$ and phenanthroline were present in the initial solution.

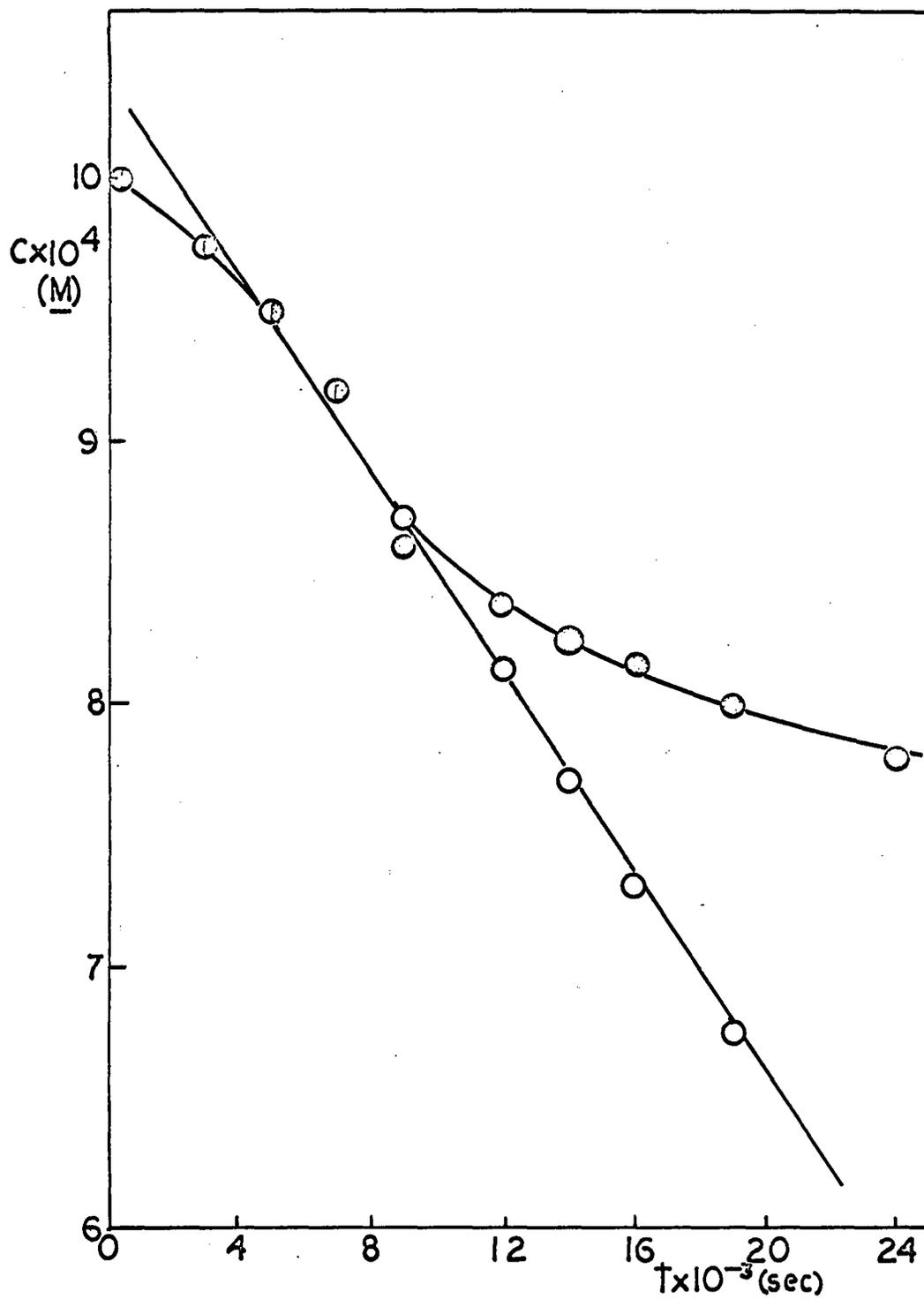


Figure 18. The Rate of Disappearance of 1,10-Phenanthroline Versus Time at 45° C in 50% Diglyme

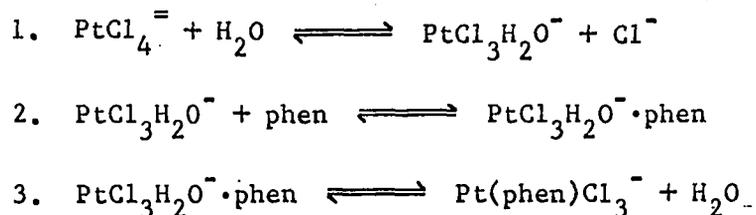
CHAPTER 5

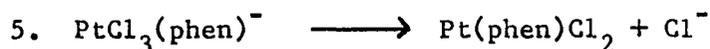
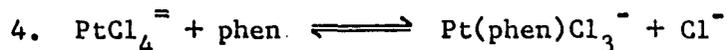
CONCLUSIONS

It seems very unlikely that a single mechanism could be proposed to account for the widely different results obtained when studying the reaction in water and in mixed solvent systems. Therefore, a separate mechanism will be proposed for each of the two cases, and any similarities between them will be discussed in the concluding paragraphs.

The Aqueous Reaction

The reaction of $\text{PtCl}_4^{=}$ with 1,10-phenanthroline seems to proceed via a mechanism very similar to the mechanisms proposed for other plus-two transition metal ions. Several unusual features of the reaction distinguishes it from similar reactions so far studied. It is considerably slower than reactions involving other plus-two ions and phenanthroline. The observed rate is second-order, first-order in both ligand and metal complexes. These facts and others discussed in the results section seem to be best explained by the following mechanism:





The first step gives an aquo-platinum complex, which is more labile than the tetra-chloroplatinate, and chloride ion, in a reversible reaction. The second step involves the formation of an outer-sphere complex (30-38). If this is true, then $k_{\text{H}_2\text{O}}$, the observed second-order rate constant, is a composite value; e.g., $k_{\text{obs}} = K_0 k_2$, where k_2 is the rate constant for the water exchange and K_0 is the formation constant for the outer-sphere complex. Using a value of $4.8 \times 10^{-5} \text{sec}^{-1}$ for k_2 , obtained by assuming the chloride exchange rate is controlled by the rate of water exchange, K_0 was calculated to be 230M^{-1} . Use of equation I (50) for the reaction of $\text{PtCl}_4^{=}$ with phenanthroline ion, discussed in the Introduction, gave $K_0 = 250 \text{M}^{-1}$. While both methods are approximations at best, the results seem to be in reasonable agreement with values obtained by others (38, 39, 41).

The fourth step involves the direct reaction of $\text{PtCl}_4^{=}$ and phenanthroline. This step may actually involve several steps whose combined rate would be k_{Cl} and whose overall process is first-order in both reactants. The final step, coordination of the second nitrogen, must be fast in contrast to the other steps.

The short induction period observed in the reaction may be explained by this mechanism. Since steps two and three have a shorter half-life than step four under the reaction conditions used, the majority of the reaction follows this path. However, this path requires an initial concentration of $\text{PtCl}_3\text{H}_2\text{O}^-$. At $t = 0$, the concentration of the

aquo complex is zero and builds up to near the equilibrium concentration in about 1000 seconds or about three half-lives. Once the equilibrium concentration is approached the path denoted by 2 and 3 proceeds in the normal manner.

The chloride ion dependence is explained by steps one through four. The reaction would proceed through both PtCl_4^- and a solvated species $\text{PtCl}_3\text{H}_2\text{O}^-$ at different rates, k_{Cl} and $k_{\text{H}_2\text{O}}$.

An attempt was made to separate the rate constants, k_{Cl} and $k_{\text{H}_2\text{O}}$, involved, assuming the proposed mechanism:

$$1. \text{ rate} = k_o [\text{PtCl}_4^-] [\text{phen}] = k_{\text{Cl}} [\text{PtCl}_4^-] [\text{phen}] \\ + k_{\text{H}_2\text{O}} [\text{PtCl}_3\text{H}_2\text{O}^-] [\text{phen}]$$

$$2. k_o [\text{PtCl}_4^-] = k_{\text{Cl}} [\text{PtCl}_4^-] + k_{\text{H}_2\text{O}} [\text{PtCl}_3\text{H}_2\text{O}^-]$$

If equilibrium is established between PtCl_4^- and $\text{PtCl}_3\text{H}_2\text{O}^-$,

then

$$3. [\text{PtCl}_3\text{H}_2\text{O}^-] = K \frac{K [\text{PtCl}_4^-]}{K + [\text{Cl}^-]} \text{ and}$$

$$4. \frac{k_{\text{H}_2\text{O}} K + k_{\text{Cl}} [\text{Cl}^-]}{K + [\text{Cl}^-]} = k_o$$

At different chloride concentrations the term $k_{\text{H}}K$ does not vary. Therefore:

$$5. k_{o_1} (K + [\text{Cl}^-]_1) - k_{o_2} (K + [\text{Cl}^-]_2) = k_{\text{Cl}} [\text{Cl}^-]_1 - k_{\text{Cl}} [\text{Cl}^-]_2$$

or, rearranging:

$$6. \frac{k_{o1}(K + [Cl^-]_1) - k_{o2}(K + [Cl^-]_2)}{[Cl^-]_1 - [Cl^-]_2} = k_o$$

Rearranging equation 4 gives:

$$7. k_{H_2O} = \frac{k_o(K + [Cl^-]) - k_{Cl}[Cl^-]}{K}$$

or

$$8. k_{H_2O} = k_o + \frac{(k_o - k_{Cl})[Cl^-]}{K}$$

The values of k_{Cl} and k_{H_2O} calculated from the observed rate constant at chloride concentrations ranging from 0.1 to $10 \times 10^{-2} M$ are given in Table XIII.

TABLE XIII

RATE CONSTANTS AND % k_o FOR THE TWO PATHS OF THE REACTION OF $PtCl_4^{2-}$ WITH 1,10-PHENANTHROLINE UNDER VARIOUS CONDITIONS

$10^3 k_{Cl}$	$10^3 k_{H_2O}$	$10^2 [Cl^-]$	$10^2 k_o$	% k_o (path 1)	% k_o (path 2)	T° C
4.00	11.55	0.1	11.2	1.4	99	45
3.60	11.45	1.0	9.35	11	88	
3.67	11.32	2.0	8.08	20	78	
3.60	11.63	4.0	6.80	33	67	
3.70		10.0	5.25	44	56	
3.85		2.0	11.2 ^a	21	79.5	
6.6	26.0	2.0	26.4 ^a	8.1	90.5	65

a. $u = 2.3 \times 10^{-2}$

Also given is the percent of k_o for each path calculated from the following two steps:

$$1. \quad \%k_o = \frac{k_{Cl} [Cl^-]}{K + [Cl^-]}$$

$$2. \quad \%k_o = \frac{k_{H_2O}K}{K + [Cl^-]}$$

Figure 13 is a plot of k_o versus chloride ion concentration calculated from the average values for k_{H_2O} and k_{Cl} . The limiting values of the graph must be k_{H_2O} and k_{Cl} , respectively. The experimentally determined values of k_o are shown as circles. At chloride ion concentrations in the range 2×10^{-2} to $0.1 \times 10^{-2} M$, the reaction proceeds mainly by the solvent intermediate path. The acid dependence has been discussed in the chapter on results. This discussion is incorporated into the mechanism.

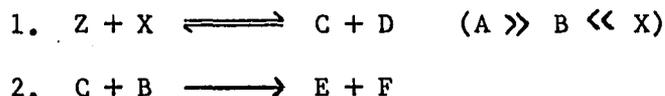
Changes in the entering ligands affect the overall rate of the reaction but not the observed kinetic path. The much less rigid ligands could react faster simply because of steric factors. Their flexibility allows easier access to the complex. The outer-sphere complex equilibrium constant would be expected to change as the ligand changed, as would both k_2 and k_{Cl} . A decrease of 5% in the value of K_o would account for the observed rate increase in the reaction between the 4,7-dimethyl derivative and the tetrachloroplatinate ions. Combining relatively small changes in these parameters easily accounts for the observed results.

An increase in ionic strength caused a decrease in the rate of reaction. The calculated charge product (-1.96) was indicative of a doubly-charged negative ion playing an important part in the rate step of the reaction. There are two possible explanations for this result. First, the Debye-Huckel limiting law used to calculate the value is applicable only at concentrations in the 10^{-3} M and lower range. The concentrations used in these experiments were in the range 10^{-1} M to 2×10^{-2} M. This could have caused large errors in the calculated charge product. Secondly, increasing the ionic strength could have inhibited the formation of the $\text{PtCl}_3\text{H}_2\text{O}^-$ ·phenanthroline outer-sphere complex, forcing a larger percentage of the reaction to follow the path controlled by k_{Cl} . This inhibition could be caused by the formation of stable ion pairs between the $\text{PtCl}_3\text{H}_2\text{O}^-$ and some added cation, such as NH_4^+ or K^+ .

This mechanism adequately accounted for the observed behavior of the reaction under all of the conditions studied. It is consistent with mechanisms proposed for similar reactions involving a wide variety of ligands and metals. Further studies may modify or eliminate certain steps, specifically steps two and three. Unfortunately it was not possible to study either the rate of water exchange or outer-sphere complex formations because of experimental difficulties. It must be noted that an $\text{S}_\text{N}2$ mechanism would also explain the observed results. At the present time it is impossible to distinguish between these two mechanisms.

The Reaction of K_2PtCl_4 with 1,10-Phenanthroline
in Mixed Solvents

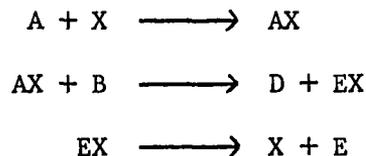
The few zero-order reactions studied to date seem to react via one of two mechanisms. One mechanism in which the disappearance of a reactant follows a zero-order rate law is (63):



(A and B, the reactants; E and F, the observed products)

In this case step two is completed before step one has made a significant change in the concentration of A. While X might be solvent, in the reaction of 1,10-phenanthroline with tetrachloroplatinate ion, neither reactant was in sufficient excess to be A. It is doubtful that A and X correspond to the different parts of the mixed solvent. Also, the observed rate of the reaction depends on the initial concentration of the tetrachloroplatinate ion. This mechanism does not explain that dependence.

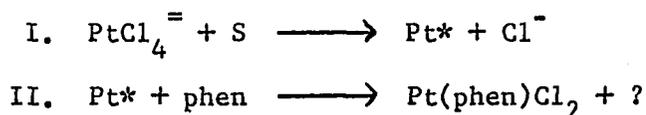
The second mechanism usually proposed to account for zero-order rate dependence involves the presence of some catalyst, the rate being dependent on the dissociation of the product from the catalyst:



Here X is present in limited amounts. It is usually a surface catalyst (64) or sometimes a very labile metal complex (60).

To account for the results in this case the catalyst must be one of the following: the walls of the reaction vessel; some impurity present in one of the reactants or the solvent; or a combination of the above. Since the reaction was not zero-order in water and the rate in alcohol was not affected by changing reaction vessels, wall effects may be ruled out. The impurities most likely to be present in the K_2PtCl_4 , platinum metal and platinum(0) complexes, caused virtually no change in rate. Impurities present in the phenanthroline could not be the catalyst because changes in the concentration of the phenanthroline did not cause any change in rate. Both 95% and absolute alcohol were used and did not change the rate. Also, switching to a different solvent, such as methanol or dioxane, did not change the kinetics, indicating a solvent impurity was not the catalyst. Finally, this mechanism does not account for the observed dependence on chloride ion.

Since all other possibilities are ruled out, the rate step(s) must involve some complex solvolysis reaction. This reaction could be followed by a much faster one in which the 1,10-phenanthroline is incorporated into the platinum complex. This may be illustrated by the reactions:



In these reactions, reaction I is probably a complex series of reactions whose overall rate is zero-order. Pt^* is the product of

solvolysis of $\text{PtCl}_4^=$. If reaction II were fast and nearly irreversible, the reaction would not show a phenanthroline dependence.

In order to explain the rate dependence of the reaction on the initial concentration of the K_2PtCl_4 , consider two reactions, identical except that one contains twice as much K_2PtCl_4 and phenanthroline as the other. After the reaction containing the higher concentrations of reactants has completed one half-life, the reactant concentrations will equal the initial concentrations of the second reaction. However, the concentration of some reactive intermediate will be higher since it has had longer to form. This results in a faster rate for the first reaction than for the second.

As the concentration of the alcohol is increased, the solvated complex is produced more quickly, resulting in the observed rate dependence. The observed kinetic isotope effect might be due to an increased labilization of the Pt^* . The rate dependence of the reaction on chloride ion concentration may be explained by chloride ion forcing the solvolysis reaction back toward the starting material.

At the present time it is not possible to propose more than this general mechanism for the substitution reaction of 1,10-phenanthroline and $\text{PtCl}_4^=$ in the mixed solvent systems. This mechanism and the outer-sphere complex mechanism proposed for the reaction in water both require a solvolysis step, then reaction of the solvated complex with 1,10-phenanthroline. As further data are gathered concerning the nature of the solvolysis reaction of $\text{PtCl}_4^=$ in mixed solvents, it will be possible to refine the mechanism proposed for the substitution.

reaction. At that time it may become possible to compare the two mechanisms and explain the radical change in kinetics that was observed. Now it is only possible to conclude that both reactions probably involve the formation of a solvated complex as an important part of the mechanism and the observed effect in mixed solvents is not due to the presence of any catalyst except some solvated platinum complex.

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