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The Preparation and Kinetics of Sterically Hindered Gold (III) Complexes

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UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

THE PREPARATION AND KINETICS
OF STERICALLY HINDERED
GOLD (III) COMPLEXES

This thesis is submitted to the Committee of Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

by David L. ^{Author}Fant, ^mM.S. 1972

By David L. Fant

Approved Charles F. Wack
Thesis Advisor

Approved W. W. Winkler
Committee on Graduate Studies

Date 6-10-72



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To my wife, Pamela, and to my family, whose encouragement and understanding made this work possible, this thesis is gratefully dedicated.

ACKNOWLEDGEMENT

I wish to express my thanks to Professor Charles F. Weick, my Research Advisor, for suggesting this topic and for his many hours and evenings which were given in guidance, assistance and encouragement in its completion.

I also wish to acknowledge the loan of the Polaroid Oscilloscope Camera from the Electrical Engineering Department of Union College.

TABLE OF CONTENTS

Acknowledgements.....	iii
List of Figures.....	v
List of Tables.....	vi
Abstract.....	vii
List of Abbreviations.....	viii
Introduction.....	1
Experimental.....	5
Materials.....	5
Analysis.....	5
Preparation of Complexes.....	7
Kinetic Studies.....	10
Results and Conclusions.....	21
Summary.....	30
References.....	31
Bibliography.....	33

LIST OF FIGURES

Figure	Page
1. Absorbance of AuCl_4^- vs Au Concentration	6
2. Absorption Spectra of $[\text{Au}(\text{Me}_2\text{dien-H})\text{Br}]^+$	12
3. Comparison of Absorption of Bromo and Chloro species of $[\text{Au}(\text{Et}_2\text{dien-H})\text{X}]^+$	13
4. Oscilloscope trace of Reaction of $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ with 0.05 M Br^-	16
5. Observed Rate Constants for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ vs Bromide Concentration	18
6. Observed Rate Constants for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ vs Bromide Concentration	19
7. Observed Rate Constants for $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ vs Bromide Concentration	20

LIST OF TABLES

Table		Page
I	Pseudo First Order Rate Constants	22
II	Rate Constants; First and Second Order	23
III	Relative First and Second Order Rate Constants	25
IV	Ratio of Rate Constants for Pairs of Complexes	26

ABSTRACT

Past studies indicate that $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ reacts with bromide as a pseudo octahedral complex while $[\text{Au}(\text{dien-H})\text{Cl}]^+$ reacts by the bimolecular mechanism expected for square planar complexes.

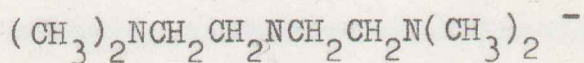
The purpose of this research was to prepare and study complexes with steric hindrance greater than that of the dien complex but less than that of the Et_4dien complex. Complexes of Me_2dien , Me_4dien , and Et_2dien with gold(III) were prepared and investigated.

Rates observed indicate that all of the complexes studied react by the expected bimolecular mechanism. In addition to retardation of the reaction by steric effects, retardation by electronic effects was observed.

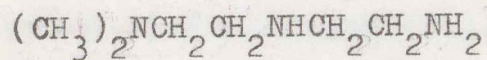
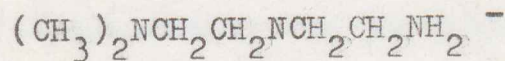
LIST OF ABBREVIATIONS

The following abbreviations will be used throughout the text of this paper:

<u>Abbreviation</u>	<u>Name & Formula</u>
amine	any dien or substituted dien
amine-H	the conjugate base of amine
dien	diethylenetriamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
dien-H	the conjugate base of dien $\text{NH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2^-$
Et ₄ dien	1,1',7,7'- tetraethyldiethylene- triamine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$
Et ₄ dien-H	the conjugate base of Et ₄ dien $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2^-$
Et ₂ dien	1,1' diethyldiethylenetriamine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
Et ₂ dien-H	the conjugate base of Et ₂ dien $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2^-$
Me ₄ dien	1,1',7,7' tetramethyldiethylene- triamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$

Me₄dien-Hthe conjugate base of Me₄dienMe₂dien

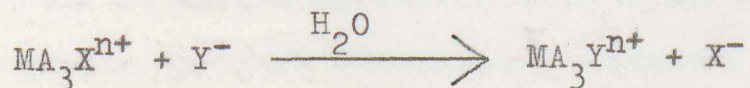
1,1'-dimethyldiethylenetriamine

Me₂dien-Hthe conjugate base of Me₂dien

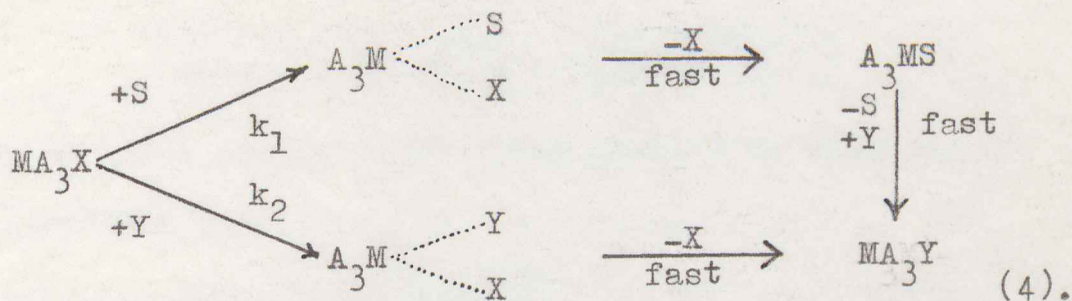
INTRODUCTION

During the past decade, extensive quantitative studies have been made on square planar, low spin d^8 systems, especially those of Pt(II) and Pd(II). (1). Recently a considerable effort has been devoted to the investigation of the kinetics and the mechanism of the Au(III) system (2),(3).

Square planar substitution reactions of the form:



are believed to follow a bimolecular displacement mechanism which can be represented as:



The bimolecular nature of both of the above reaction paths is supported by four types of evidence: (a) for non symmetric species, steric configuration is retained; (b) five (and six) coordinated d^8 systems are known to exist and have been isolated; (c) the

rates of substitution are dependent on the concentration of the entering nucleophile; and (d) the presence of large groups above and below the plane of the ion has been shown to decrease the rate of substitution, presumably because attack by the entering nucleophile is blocked (5). The presence of a vacant p_z orbital in these low spin d^8 complexes supports the reasonableness of this mechanism since this orbital can accept a pair of electrons from the entering ligand and thus create the five coordinated, trigonal bipyramidal intermediate required. This mechanism follows the two term rate law:

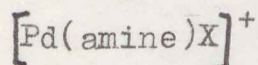
$$\text{Rate} = k_1 [\text{MA}_3\text{X}^{n+}] + k_2 [\text{MA}_3\text{X}^{n+}] [\text{Y}^-]$$

which under pseudo first order conditions with excess Y^- reduces to:

$$\text{Rate} = k_{\text{obs}} [\text{MA}_3\text{X}^{n+}]$$

where $k_{\text{obs}} = k_1 + k_2 [\text{Y}^-]$ (6).

The rate of substitution reactions for certain sterically hindered Pd(II) complexes of the type



(where amine = Et_4dien , MeEt_4dien , or Me_5dien ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) with various nucleophiles has been shown

to be independent of the nucleophile concentration and exhibits a kinetic behavior similar to octahedral complexes (7). This same nucleophile independence has also been observed for $[\text{Pt}(\text{Et}_4\text{dien})\text{Cl}]^+$ and $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ (8),(9).

While the bromide substitution reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ proceeds at a rate which is independent of the nature and concentration of the nucleophile, the substitution reaction of $[\text{Au}(\text{dien-H})\text{Cl}]^+$ proceeds at a rate which is strongly dependent upon the concentration and the nature of the entering ligand (k_2 range from approximately 0 to $6100 \text{ M}^{-1} \text{ sec}^{-1}$) (10). In view of these two extremes of ligand dependence, it was decided to investigate several less sterically hindered $[\text{Au}(\text{amine})\text{Cl}]^{2+}$ complexes to determine the level of steric hindrance necessary to cause entering nucleophilic independence. The choice of Au(III) complexes in place of Pt(II) or Pd(II) complexes was dictated by the relative reaction rates of these three ions. $[\text{Pd}(\text{dien})\text{Cl}]^+$ was found to react at a rate too rapid to measure, while $[\text{Pt}(\text{Et}_4\text{dien})\text{Cl}]^+$ required that the reaction be studied at 80°C to obtain rate data in a reasonable length of time (11),(12). However, rate data for both $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$ and

$[\text{Au}(\text{dien})\text{Cl}]^{2+}$ have been obtained and measured at 25°C (13), (14). Since these two complexes represent two extremes, it was expected that other substituted diethylenetriamine complexes of Au(III) would react at measurable rates.

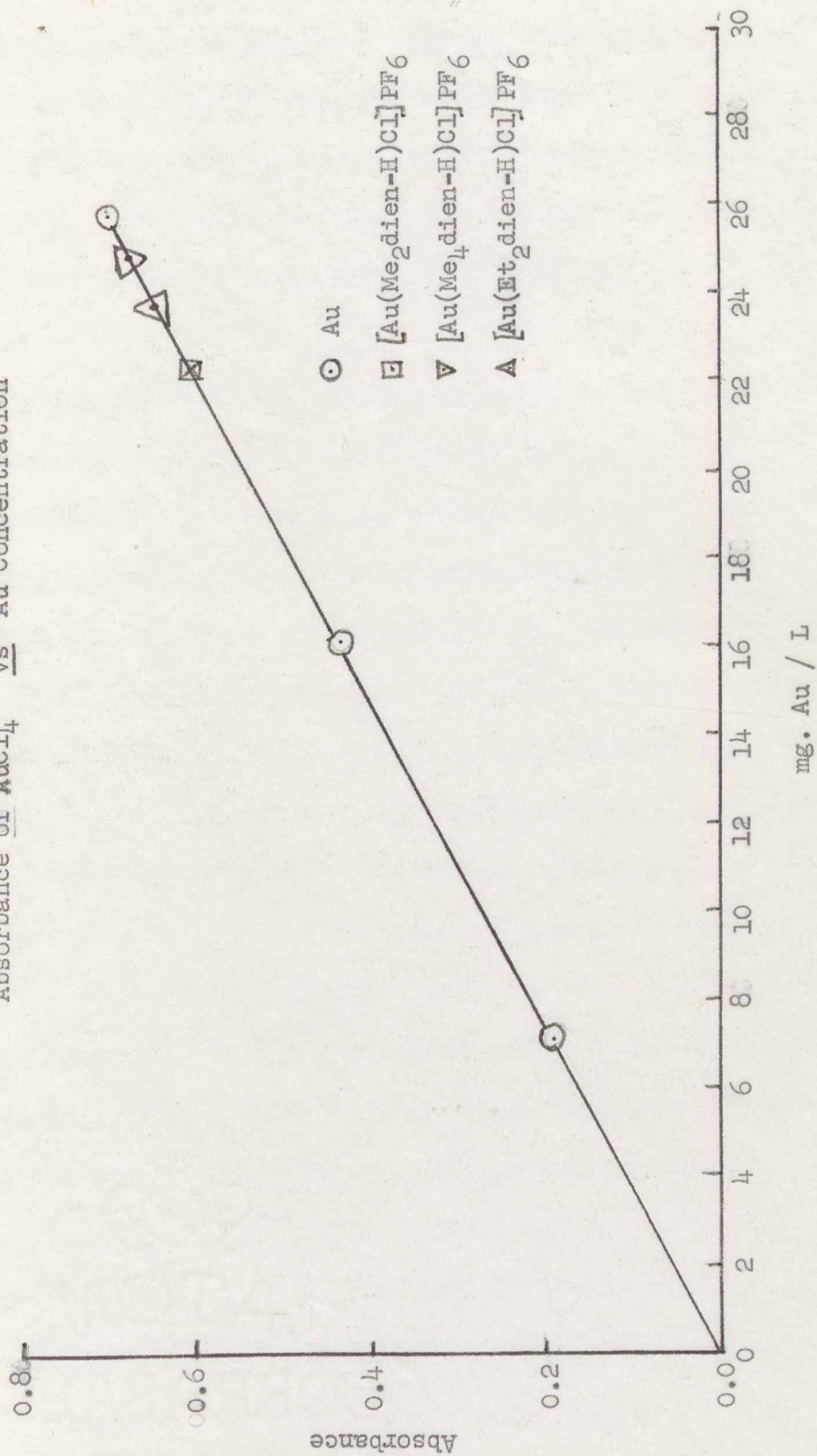
EXPERIMENTAL

Materials: Fine gold powder was obtained from Alfa Inorganics, Inc.. The substituted diethylene-triamines were obtained from Ames Laboratory, and the hexafluoroammoniumphosphate was obtained from Alfa Inorganics, Inc.. All other chemicals used were reagent grade.

Analyses: Complexes, which were prepared as the hexafluorophosphate salt, were analysed for gold content by dissolving an accurately weighed amount in aqua regia followed by repeated evaporation with HCl to remove NO_2 . Extreme care was necessary throughout the evaporation to insure that the solutions did not evaporate to dryness. Reproducible results were not obtained if the solutions were reduced to dryness, presumably due to the volatilization of Au in the presence of PF_6^- (15). The solutions of HAuCl_4 thus obtained were quantitatively diluted to a final concentration of approximately 10^{-4} molar. The absorbance of these solutions was obtained at 314 nm. using a Beckman DK-2 spectrophotometer. The concentration of gold was then obtained from a standard absorbance curve prepared from a solution of HAuCl_4 obtained from pure gold (Figure 1).

FIGURE 1

Absorbance of AuCl_4^- vs Au Concentration



Preparation of Complexes: HAuCl_4 was prepared by dissolving a quantity of gold metal in a few ml of aqua regia followed by repeated evaporation with HCl to remove NO_2 . When the volume was reduced to 1-2 ml, the solution was allowed to cool and crystals of HAuCl_4 formed.

$[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]\text{PF}_6$: HAuCl_4 equivalent to one gram of gold was dissolved in 5 ml of ice cold ether. This was added dropwise with stirring to a solution containing 5 ml of 1,1'-diethyldiethylenetriamine in 15 ml of ice cold ether. Throughout the addition of the HAuCl_4 , the reaction mixture was maintained at a temperature of less than 5°C by use of a Stir Kool, Model SK 12, manufactured by Thermoelectrics Unlimited, Inc.. An orange grease or paste formed during the addition of the HAuCl_4 . This paste was washed with three 10 ml portions of ice cold ether. The paste was then dissolved in 15 ml of iced water and the excess dien removed by extracting the aqueous solution of the complex with ten 30 ml portions of ice cold ether. One gram of NH_4PF_6 was added and the aqueous solution allowed to freeze in a dry ice - acetone bath. The frozen mixture was then allowed to thaw under running water with vigorous agitation. The red crystals

which formed in the flask were collected by filtration and recrystallized from ethanol. The final product was collected on filter paper, washed first with ethanol, then with ether and dried in a desiccator containing CaCl_2 . The product was stored in a refrigerator. A yield of 32.3% (based on the weight of gold) was obtained.

Analysis: Calculated for $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]\text{PF}_6$:
Au 36.8%; Found: Au 36.5%.

$[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]\text{PF}_6$: The procedure used for the preparation of $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]\text{PF}_6$ was similar to that employed for $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]\text{PF}_6$ with the exception that an oil formed rather than crystals when the frozen mixture thawed. An additional 1.5 grams of NH_4PF_6 was added, the mixture allowed to freeze again in dry ice and acetone. This frozen mixture was reduced in volume on a Buchler Instruments Flash Evaporator, Model No. PF -10DN. When the volume of the solution was reduced to one half of its original volume, bright red crystals formed which were collected on a filter paper. The crystals were recrystallized from ethanol using the Flash Evaporator and dried over CaCl_2 . The yield was 25.4% based on the weight of gold used.

Analysis: Calculated for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]\text{PF}_6$:
Au 38.6%; Found: 38.6%.

$[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]\text{PF}_6$: This material was prepared in the same manner as the $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]\text{PF}_6$. This material was recrystallized from a solution of 70 % ethanol in acetone using the Flash Evaporator. The red crystals which formed were washed with absolute alcohol and dried over CaCl_2 . The yield was 32.6% based on the weight of gold used.

Analysis: Calculated for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]\text{PF}_6$:
Au 36.6%; Found: Au 36.8%.

KINETIC STUDIES

Previous studies of the aqueous solution chemistry of $[\text{Au}(\text{dien-H})\text{Cl}]^+$, $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$, and $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ have indicated that: (a) these complexes undergo extensive hydrolysis in neutral aqueous solutions; (b) an excess of halide ion represses hydrolysis of these complexes within certain pH ranges; (c) the conjugate acids of these complexes are stable in perchloric acid; and (d) the conjugate acids of these complexes undergo decomposition in hydrohalic acids (16),(17),(18).

Since the aqueous solution chemistry of the above complexes is so similar, the aqueous solution chemistry of $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ and $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ was briefly examined to determine the behavior of the complexes at various pH's.

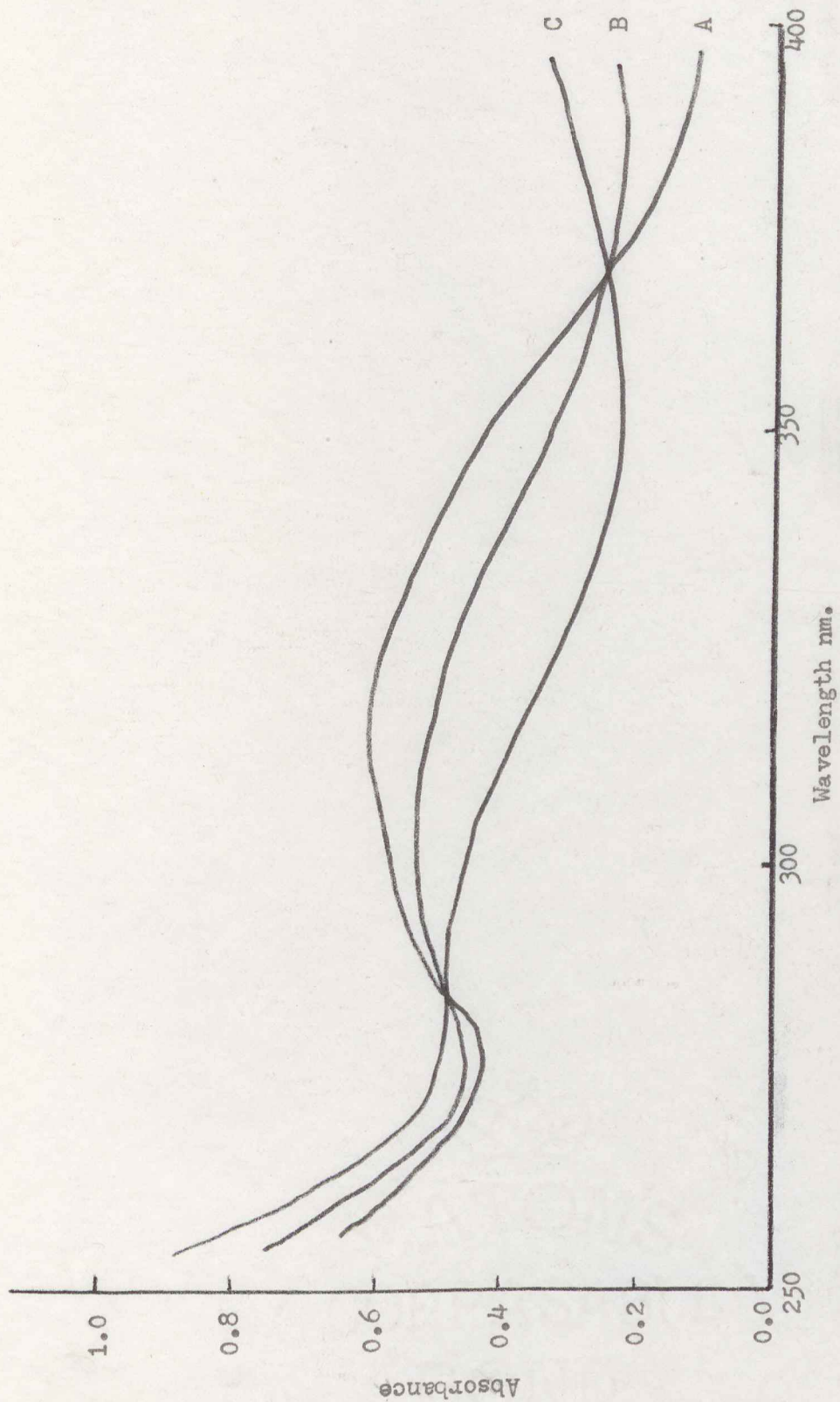
In each case, a portion of the complex was dissolved in a small volume of H_2O and adjusted to a pH of 9 - 10 with 1N NaOH. This solution was passed through a Dowex I-X-8 ion exchange resin previously converted to the OH^- form, to place the complex in the form $[\text{Au}(\text{amine-H})\text{OH}]^+$. The effluent from the column was collected in a volumetric flask and diluted to volume. To this solution was added

sufficient Br^- to make the solution 0.5 M Br^- . This solution was placed in a water jacketed beaker and maintained at 25°C by circulating water through the jacket from a P.M. Tamson constant temperature bath. The pH of this solution was measured with a Fisher Accumet pH Meter previously calibrated using Beckman 6.8 buffer. The spectrum of this solution was scanned repeatedly at various pH's using a Perkin Elmer Model 202 UV-Visible Spectrophotometer. The pH was adjusted by use of NaOH and HClO_4 . Figure 2 shows the curves obtained for the Me_2dien complex.

The studies indicated that at a pH greater than 7.7 the solution consists of a mixture of $[\text{Au}(\text{amine-H})\text{OH}]^+$ and $[\text{Au}(\text{amine-H})\text{Br}]^+$. At a pH of less than 5.5 the complex is in the form of $[\text{Au}(\text{amine-H})\text{Br}]^+$ and $[\text{Au}(\text{amine})\text{Br}]^{2+}$. Thus a pH range of 5.5 to 7.7 was dictated as necessary to insure that the final product of the study would be in the form of $[\text{Au}(\text{amine-H})\text{Br}]^+$.

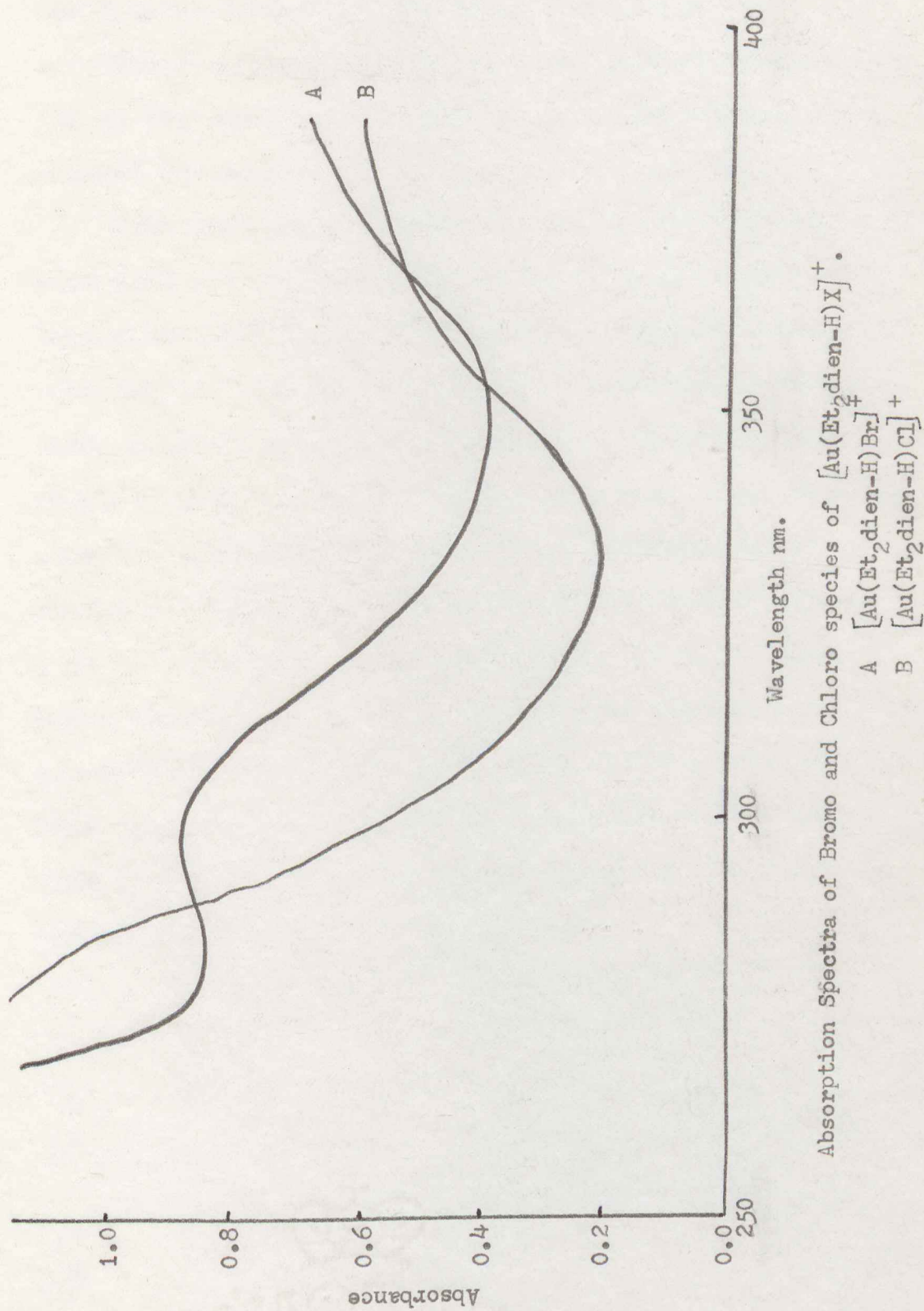
Two solutions of each complex were prepared in a pH 7 buffer with 0.5 M Cl^- present in one and 0.5 M Br^- present in the other and the spectrum of each obtained. The results for $[\text{Au}(\text{Et}_2\text{dien-H})\text{X}]^+$ are shown in Figure 3. Examination of these spectra indicate a maximum difference in absorbance at a wavelength of 310 nm. Consequently

Figure 2



Absorption Spectra of $[\text{Au}(\text{Me}_2\text{dien-H})\text{OH}]^+$ in 0.5 M Br^- as a function of pH
A. pH = 7.2; B. pH = 6.5; C. pH = 5.9.

Figure 3

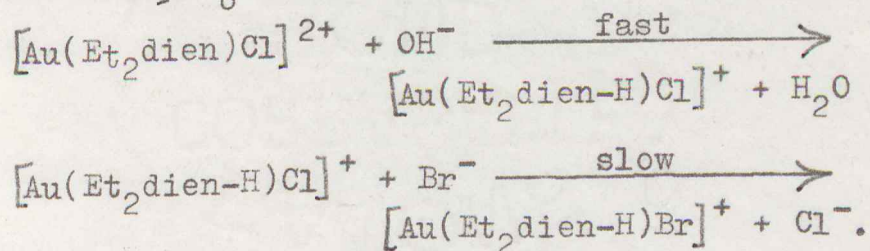


the wavelength of 310 nm was selected as optimum for the kinetic study for the Et₂dien complex.

Wavelengths of 310 nm for the Me₂dien complex and 330 nm for the Me₄dien complex were selected by a similar procedure.

Solutions of the chloro complexes in the conjugate acid form were prepared by dissolving the solid [Au(amine-H)Cl]PF₆ in 0.04 M HClO₄. Kinetic runs were carried out by allowing this solution to react with an equal volume of a solution containing the bromide ion at various concentrations. This bromide solution contained a sufficient concentration of phosphate buffer and NaClO₄ to produce, after mixing, a pH of 6.8 and an ionic strength of 0.115. Under these conditions, the Au(III) complex was instantaneously converted to the basic form of the chloro complex. This then reacted with the Br⁻ to produce the basic form of the bromo complex. The reaction sequence for

[Au(Et₂dien-H)Cl]PF₆ is as follows:

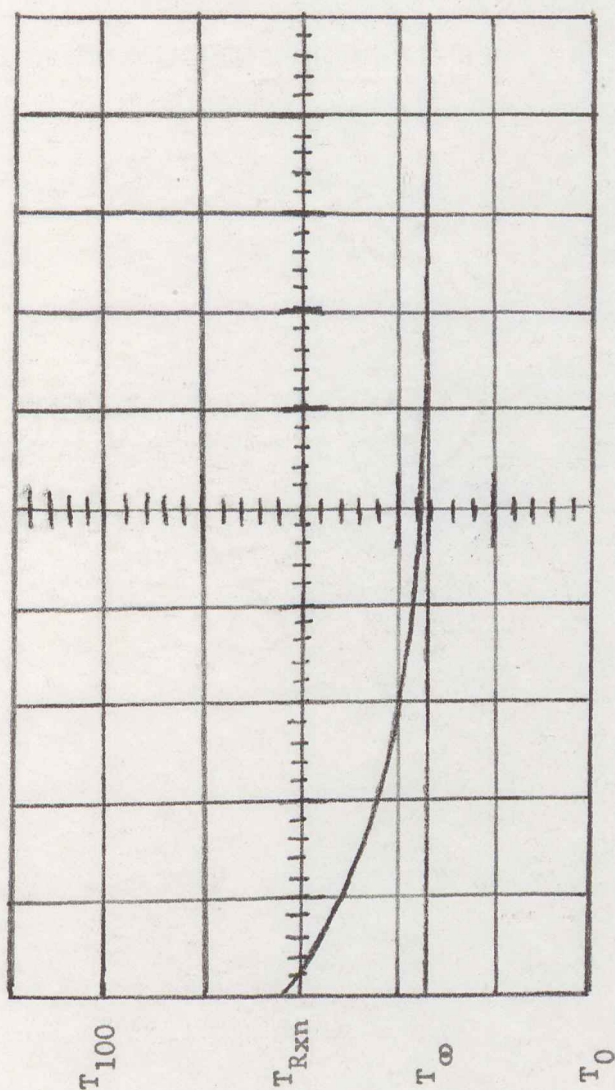


Rates were determined using an Aminco-Morrow Stopped Flow Apparatus in conjunction with the monochromator from a Beckman DU spectrophotometer. The photomultiplier output of the stopped flow apparatus was connected through an Aminco High Performance Kinetic Photometer to the vertical input of a Tektronix 531 Oscilloscope. The oscilloscope traces of change in percent transmittance as a function of time were recorded on film using a Polaroid Oscilloscope Camera. A typical trace is shown in Figure 4.

All reactions were performed at a pH of 6.8, an ionic strength of 0.115, and at a temperature of 25.0°C. The concentration of the complex in each case was 4×10^{-4} M. For all complexes, bromide concentrations of 0.05 M, 0.01 M, and 0.005 M were used. Additionally, $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ was studied at 0.001 M bromide ion concentration. For each complex, replicate runs were performed at each concentration level. Reproducibility was better than 1% transmittance. To prevent instrument drift, the photometer output was set such that a 5 volt output was equivalent to 100% transmittance (19).

The percent transmittance values obtained from

Figure 4



Typical Oscilloscope Trace for Reaction of $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ with 0.05 M Br^- . T_{100} = 100% Transmittance; T_0 = 0% Transmittance; T_{Rxn} = Transmittance of Reaction; T_{∞} = Reaction transmittance at infinite time.

the photographic traces were converted to absorbance values. The difference in absorbance at time "t" (A_t) and at the completion of the reaction (A) was obtained and the log of the difference plotted as a function of time. From this linear plot the slope, or pseudo first order rate constant, was calculated for the specific bromide concentration under study. Plots of replicate runs yielded slopes which agreed within 10%. A plot of the observed rate constants as a function of the bromide ion concentration yielded a straight line with an intercept equal to k_1 , or the solvent path rate constant, and a slope of k_2 for the bromide path. (Figure 5,6,7).

Figure 5

Observed Rate Constant for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$
versus Bromide Concentration @ $T = 25.0^\circ\text{C}$

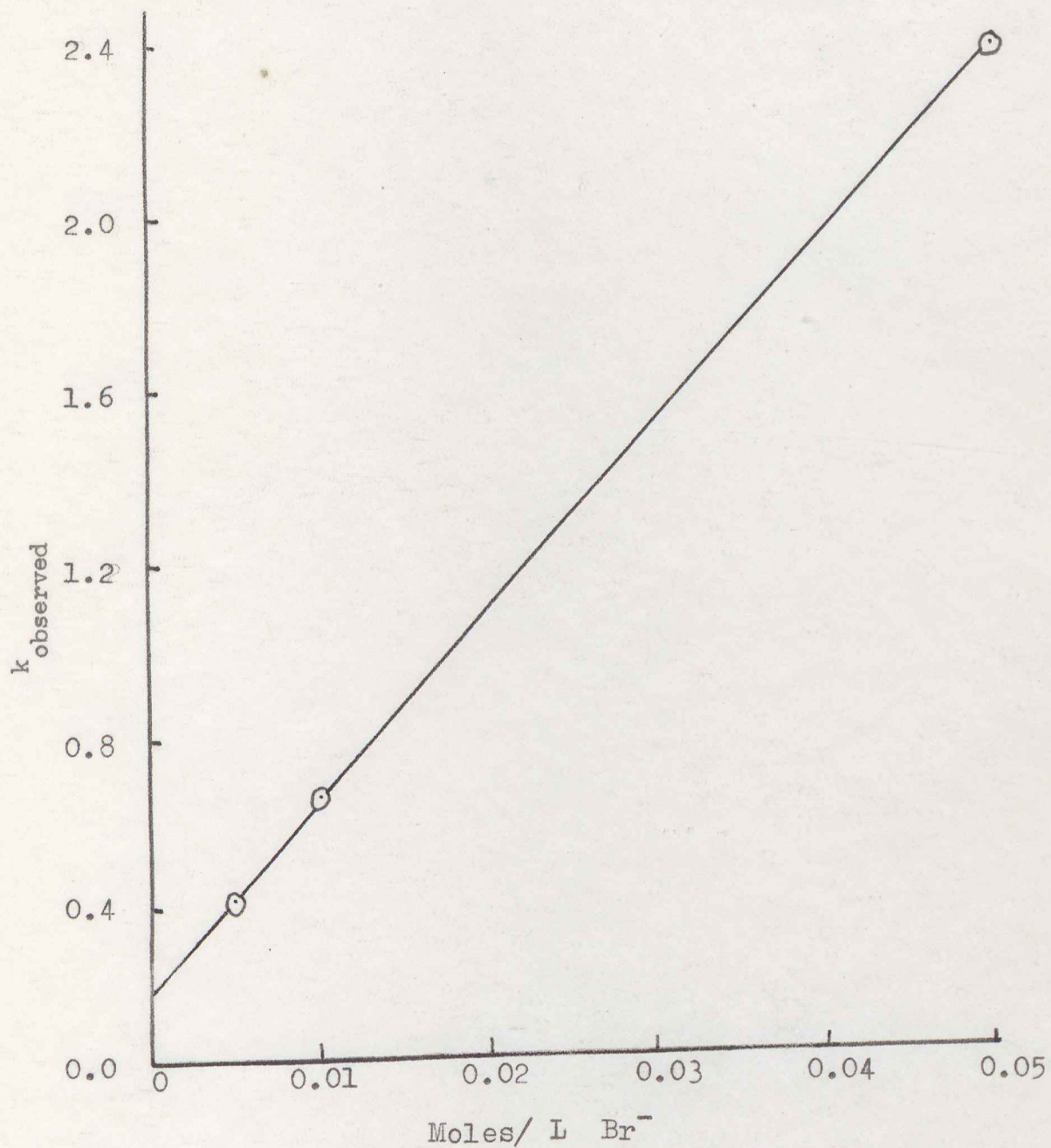


Figure 6

Observed Rate Constant for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$
versus Bromide Concentration @ $T = 25.0^\circ\text{C}$

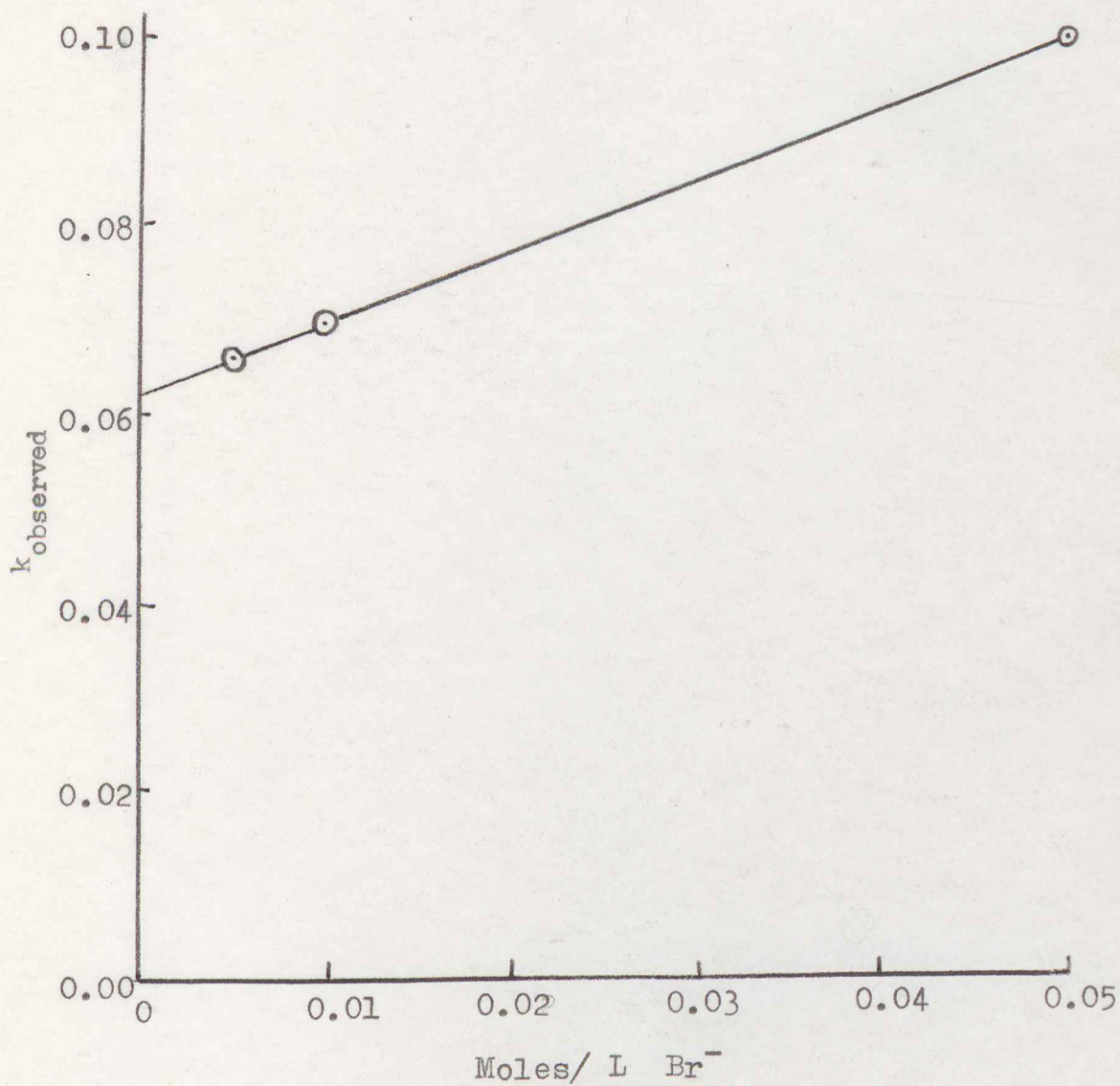
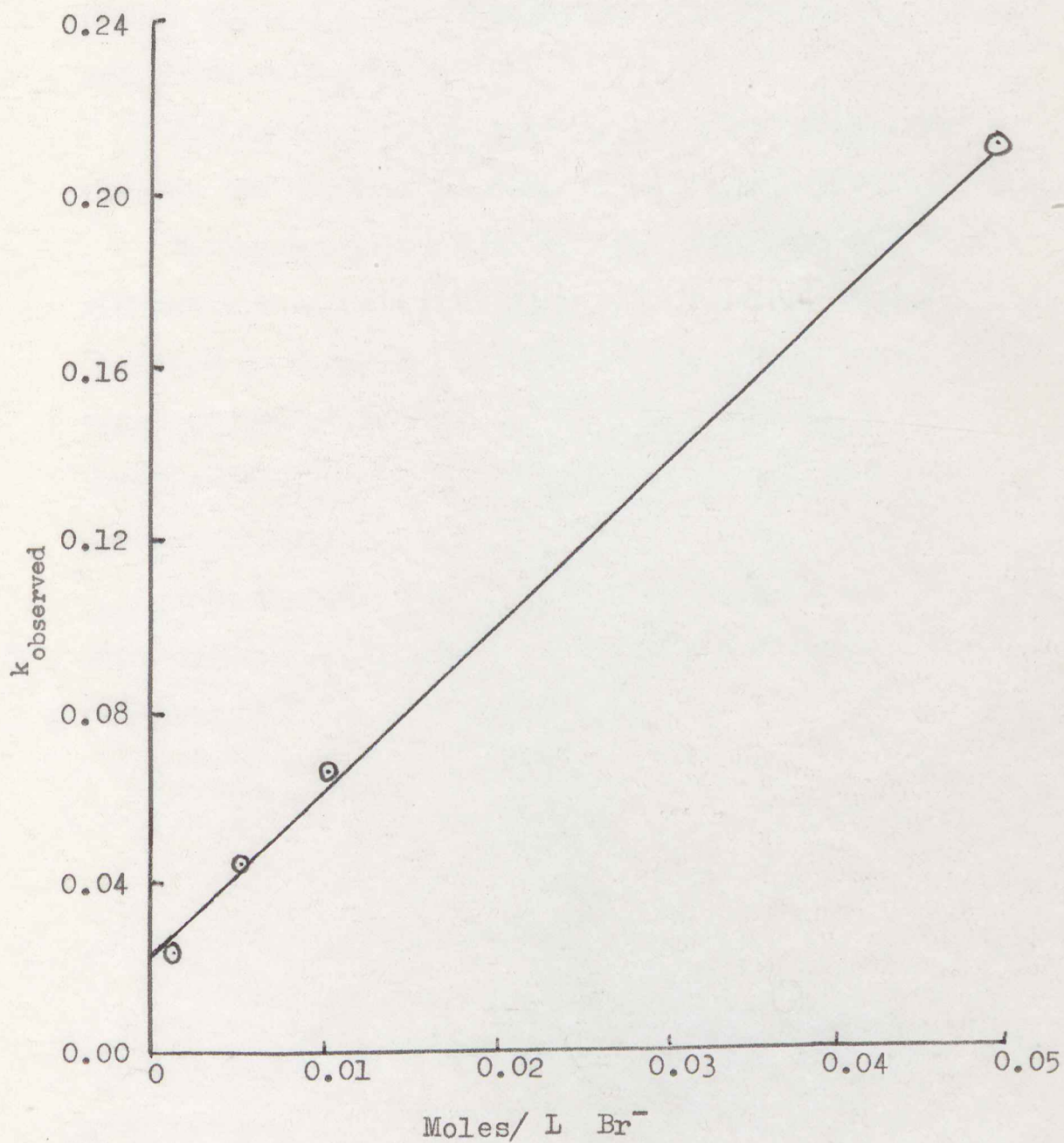


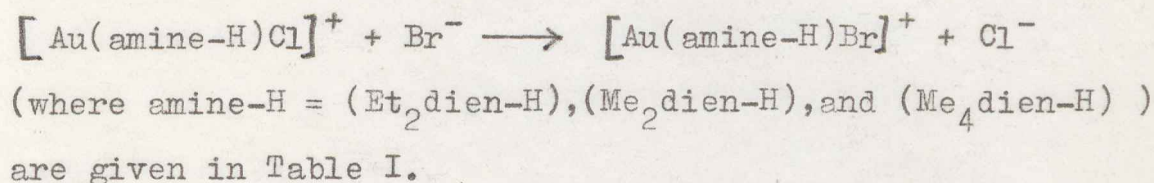
Figure 7

Observed Rate Constant for $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$
versus Bromide Concentration @ $T = 25.0^\circ\text{C}$



RESULTS AND CONCLUSIONS

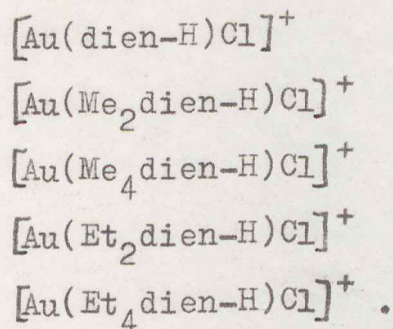
The pseudo first order rate constants obtained for the reaction:



The values of k_{obs} are reproducible within 10% and are the average of from four to eight replicate runs.

Estimated values of the rate constants for the solvent and the bromide paths are listed in Table II. Included in Table II are the data for the substitution reaction of Br⁻ for Cl⁻ in the complexes of [Au(dien-H)Cl]⁺ and [Au(Et₄dien-H)Cl]⁺ for the purpose of comparison.

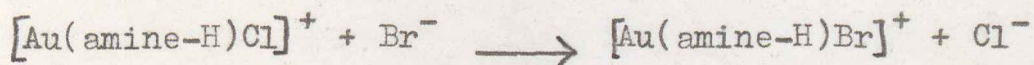
Examination of molecular models indicates that the shielding of the Au(III) by the amine increases in the following order:



In view of the proposed bimolecular substitution mechanism, one would expect a decrease in rate

TABLE I

Pseudo First Order Rate Constants for:



$$\mu = 0.115 \text{ with NaClO}_4$$
amine-H = Et₂dien-H

<u>Br⁻ concentration</u>	<u>k_{obs}</u>
0.050 M	2.1 X 10 ⁻¹
0.010 M	6.5 X 10 ⁻²
0.005 M	4.4 X 10 ⁻²
0.001 M	2.3 X 10 ⁻²

amine-H = Me₂dien-H

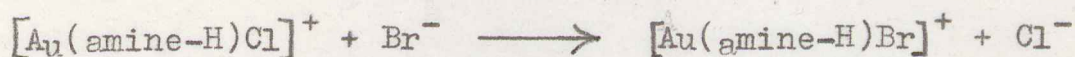
<u>Br⁻ concentration</u>	<u>k_{obs}</u>
0.050 M	2.4
0.010 M	6.9 X 10 ⁻¹
0.005 M	4.1 X 10 ⁻¹

amine-H = Me₄dien-H

<u>Br⁻ concentration</u>	<u>k_{obs}</u>
0.050 M	1.0 X 10 ⁻¹
0.010 M	7.0 X 10 ⁻²
0.005 M	6.6 X 10 ⁻²

TABLE II

Rate Constants for the Reaction:



Complex	k_1 (sec ⁻¹)	k_2 (M ⁻¹ sec ⁻¹)
$[\text{Au}(\text{dien-H})\text{Cl}]^+$	0.6 (20)	1.9×10^2 (20)
$[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$	2.0×10^{-1}	4.4×10^1
$[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$	6.2×10^{-2}	7.6×10^{-1}
$[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$	2.3×10^{-2}	3.8×10
$[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$	1.2×10^{-4} (21)	8.8×10^{-4} *

* Obtained from the slope of a plot of k_{obs} vs concentration from Reference 21.

with increasing steric hindrance for both the solvent and the bromide paths.

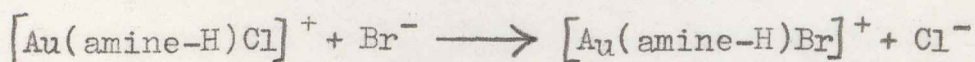
The relative rates for these five complexes are listed in Table III. It is apparent from this table that the solvent path follows the predicted order. However, an anomaly is apparent in the relative reaction rates for the bromide path in that the complexes containing $\text{Et}_2\text{dien-H}$ and $\text{Me}_4\text{dien-H}$ have exchanged positions. This anomaly can be explained by means of a combination of steric and electronic factors. A comparison of both solvent (k_1) and bromide (k_2) rate constant ratios for pairs of these complexes provides an insight into this anomaly. These ratios are listed in Table IV.

Comparing the structure of $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ to that of $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$, one would expect little difference from effects other than steric. Thus the ratio of the reaction rates should be approximately the same for both paths. As can be seen from Table IV, the rate constant ratios for both paths are approximately 10/1.

The ratios of the rate constants for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ and $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$

TABLE III

Relative First & Second Order
Reaction Rates for the Reaction:



Complex	Relative Rate k_1 ** Solvent Path	Relative Rate k_2 Reagent Path
$[\text{Au}(\text{dien-H})\text{Cl}]^+$	5000	215,000
$[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$	1660	50,000
$[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$	520	86
$[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$	192	4,300
$[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$	1	1

TABLE IV
 Ratio of Reaction Rates for
 Pairs of Complexes

	Path	
	Solvent	Reagent
$k_{(\text{Me}_2\text{dien-H})} / k_{(\text{Et}_2\text{dien-H})}$	9/1	12/1
$k_{(\text{Me}_2\text{dien-H})} / k_{(\text{Me}_4\text{dien-H})}$	3/1	580/1
$k_{(\text{Me}_4\text{dien-H})} / k_{(\text{Et}_4\text{dien-H})}$	520/1	86/1
$k_{(\text{Et}_2\text{dien-H})} / k_{(\text{Et}_4\text{dien-H})}$	192/1	4300/1

indicate that the reaction via the bromide path for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ is approximately 600 times faster than for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$. However, reaction via the solvent path is only three times faster for $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ than for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$. Since steric shielding of Au(III) should retard the reaction by both paths, the above reaction rate difference cannot be attributed exclusively to steric factors. Furthermore, molecular models do not indicate a substantial difference in the shielding of two versus four methyl groups.

The most apparent difference in the reaction paths is the charge on the attacking nucleophile. Thus, the difference in the ratios of the rate constants for the two paths can be rationalized on the basis of electronic factors. For $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ the positive charge on the Au(III) is reduced by the inductive effects of the two methyl groups on one nitrogen of the chelate ligand. For $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ the positive charge is reduced even more because of the effects of four methyl groups, two on each of the terminal nitrogen atoms of the chelate ligand. Thus, the negative bromide ion is more readily attracted to

$[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ because of a relatively larger positive charge on the central gold atom than it is to $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ with the relatively less positive gold. This decreased positive charge on Au(III) has less influence on the attack of the neutral water molecule. Thus the ratio of the bromide path rate constant should be larger than the ratio of the constants for the solvent path.

The difference in the ratio of the rate constants for the two paths for $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ and $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ can be explained in the following manner. For $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ steric hindrance almost completely prevents an attack by water. By comparison, $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ is relatively open to attack. Consequently the larger rate constant ratio for the solvent path is reasonable. The lower bromide path ratio is not completely unexpected since the $\text{Me}_4\text{dien-H}$ substituted complex has been shown to be quite slow because of the inductive effects of the four methyl groups. Thus, the low rate constant ratio results from the comparison of an already slow rate with a slower rate for $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$.

The comparison of the rate ratios for $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ and $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ presents a situation very similar to that of the complexes already listed. The relatively high solvent path ratio is expected because of the increase in steric hindrance of the $\text{Et}_4\text{dien-H}$ complex. The very large bromide path ratio is also expected because of two factors: (a) a decrease in positive charge about the central gold atom in $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$; and (b) a very low bromide path for the $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ because of the almost total shielding of the gold atom by the four ethyl groups.

SUMMARY

The relative reaction rates for the complexes studied can be explained by a combination of electronic and steric effects of the N-alkylated diethylenetriamine substituents on the central gold atom.

The overall reaction rates are decreased by increasing steric hindrance as would be expected for the square planar substituted low spin d^8 complexes of Au(III). The results also indicate that the rate of substitution by the bromide path is controlled at least in part by the variation of the positive charge on the central gold atom.

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