A Kinetic Study of the Chelate Ligand Unwrapping Reactions of Sterically Hindered Gold(III) Complexes

BY
illiam
JAMES W. THACKERAY UC 1979
III

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ABSTRACT

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The complexes $[Au(Et_2dien_{-H})Br]PF_6$, $[Au(Me_4dien_{-H})Br]PF_6$, and $[Au(Et_4dien_{-H})Br]PF_6$ have been synthesized and a kinetic study of their conjugate acids performed. This paper centers on the direct replacement of the tridentate ligand on the complex by bromide ion:

$[Au(Amine)Br]^{2+} + 3Br^- \rightarrow AuBr_4^- + AmineH_3^{3+}$ (where Amine = Et_4dien, Me_4dien, Et_2dien). A ring-opening mechanism is postulated for these reactions. The order of dependence on bromide is best explained by steric factors on each terminal nitrogen site.

LIST OF ABBREVIATIONS

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

Abbreviation	Name & Formula
amine	any dien or substituted dien
$amine_{-H}$	the conjugate base of amine
dien	diethylenetriamine $NH_2CH_2CH_2NHCH_2CH_2NH_2$
$dien_{-H}$	the conjugate base of dien $(NH_2CH_2CH_2NCH_2CH_2NH_2)^-$
Et_4dien	1,1',7,7' -tetraethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$
Et_4dien_{-H}	the conjugate base of Et_4dien $(C_2H_5)_2NCH_2CH_2NCH_2CH_2N(C_2H_5)_2^-$
Et_2dien	1,1' -diethydiethylenetriamine $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$
Et_2dien_{-H}	the conjugate base of Et_2dien $(C_2H_5)_2NCH_2CH_2NCH_2CH_2NH_2^-$
Me_4dien	1,1',7,7' tetramethyldiethylenetriamine $(CH_3)_2NCH_2CH_2NHCH_2CH_2N(CH_3)_2$
Me_4dien_{-H}	the conjugate base of Me_4dien $(CH_3)_2NCH_2CH_2NCH_2CH_2N(CH_3)_2^-$

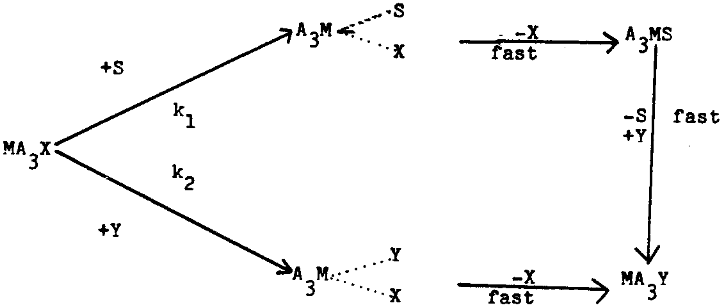
Me$_2$dien	1,1' dimethyldiethylenetriamine $(CH_3)_2NCH_2CH_2NHCH_2CH_2NH_2$
Me$_2$dien$_{-H}$	the conjugate base of Me$_2$dien $(CH_3)_2NCH_2CH_2NCH_2CH_2NH_2^-$
Me$_5$dien	1,1',4,7,7' pentamethyldiethylenetriamine $(CH_3)_2NCH_2CH_2NCH_3CH_2CH_2N(CH_3)_2$
MeEt$_4$dien	4-methyl-1,1',7,7' tetraethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2NCH_3CH_2CH_2N(C_2H_5)_2$
Me$_3$dien	1.4,7 trimethyldiethylenetriamine $(CH_3)NHCH_2CH_2N(CH_3)CH_2CH_2NH(CH_3)$
Et$_3$dien	1.4,7 triethyldiethylenetriamine $(C_2H_5)NHCH_2CH_2N(C_2H_5)CH_2CH_2NH(C_2H_5)$

INTRODUCTION

Quantitative studies have been made on square planar, low spin d^8 systems, like Pt(II), Pd(II), and Au(III).[1,2] Square planar substitution reactions of the form:

$$MA_3X^{n+} + Y^- \longrightarrow MA_3Y^{n+} + X^-$$

are believed to undergo a bimolecular displacement mechanism. The mechanism is shown below:[3]



A bimolecular mechanism is supported by the following evidence: (a) for non-symmetric species, steric configuration is retained; (b) five-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 of steric blockage of the entering nucleophile.[4] A vacant P_z orbital above and below the plane of the complex supports the trigonal bipyramidal intermediate formed by square planar complexes. This mechanism follows a two term rate law:

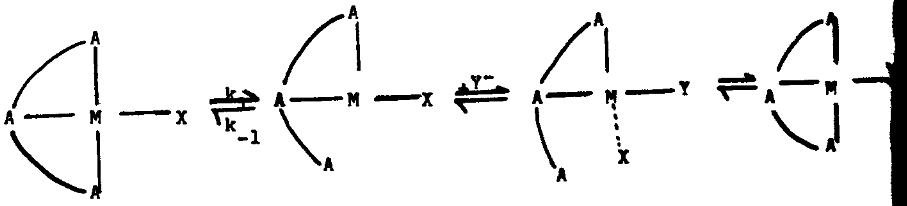
$$\text{Rate} = k_s[MA_3X^{n+}] + k_y[MA_3X^{n+}][Y^-]$$

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

$$\text{Rate} = k_{obs}[MA_3X^{n+}] \text{ (where } k_{obs} = k_s + k_y[Y^-]).^5$$

The rate of substitution for many sterically hindered Pd(II) and Au(III) complexes of the type $[M(\text{amine})X]^{n+}$ (where amine = Et_4dien, $MeEt_4$dien, or Me_5dien and their conjugate bases: X = Cl, Br, I) with various nucleophiles has been shown to be independent of the nucleophile concentration and exhibiting pseudo octahedral behavior.[6]

However, the simple square planar mechanism has been unable to explain certain anomalies in the substitution reactions of $[Au(Et_4dien_{-H})Cl]^+$, $[Pd(Et_4dien_{-H})Cl]^+$, $[Au(MeEt_4dien)Cl]^{2+}$, and $[Au(Et_2dien_{-H})Cl]^+$. For these tridentate ligand complexes, a dynamic ring opening mechanism has been suggested:



A ring opening mechanism was first proposed by Weick and Basolo to explain the anomalies found in substitution of $[Au(Et_4dien_{-H})Cl]^+$. The reaction

$$[Au(Et_4dien_{-H})Cl + X^- \longrightarrow [Au(Et_4dien_{-H})X] + Cl^-$$

(where X = Br^-, OH^-) was shown to be independent of the entering nucleophile's concentration. This behavior was considered to be caused by steric hindrance of the ethyl groups in the Et_4dien ligand. However, when X^- was the azide ion, N_3^-, the tetrabromoaurate ion formed at high azide concentrations. This side reaction occurred, it was suggested, by successive ligand unwrapping of the Et_4dien_{-H} from the Au(III) ion. These anomalies were best explained by dynamic ring opening of the tridentate ligand.[7]

Burmeister and Lim found that

$$[Pd(Et_4dien)SeCN]^+ + Br^- \longrightarrow [Pd(Et_4dien)Br]^+ + SeCN^-$$

was first order with respect to bromide. They also suggested a dynamic ring opening mechanism to relieve steric hindrance.[8]

Fant and Weick found similar steric anomalies for the rates of the reactions:

$$[Au(Amine_{-H})Cl]^+ + Br^- \longrightarrow [Au(Amine_{-H})Br]^+ + Cl^-$$

(where $Amine_{-H}$ = Me_4dien_{-H}, Et_2dien_{-H}). A ring opening mechanism was again suggested to explain a relatively fast rate for $[Au(Et_2dien_{-H})Cl]^+$.[9] Stevens (unpublished) also found for the same reaction with $[Au(MeEt_4dien)Cl]^{2+}$ that ring opening could explain relative reaction rates.[10]

Additional evidence for a ring opening mechanism for these sterically hindered Au(III) dien complexes is: (a) N-alkyl multidentate amines form less stable complexes due to steric hindrance than the corresponding N-hydrogen amines;[11] (b) Allison and Angelici found that ethyl substitution on the terminal nitrogens of dien decreases the formation constant of dien complexes of Cu(II) to a greater extent than methyl substitution at these nitrogens;[12] (c) Turan and Rorabacher have also reported such a difference in the stability of N,N-diethyl diens <u>vs</u>. N,N-dimethyl diens with Ni(II).[13]

To investigate further the importance of ring opening in the replacement reactions of Au(III) dien complexes, a quantitative kinetic study of the rate of direct replacement of the tridentate ligand by bromide was explored. The following reactions were studied:

$$[\mathrm{Au(Amine)Br}]^{2+} + 3\mathrm{Br}^- \longrightarrow \mathrm{AuBr}_4^- + \mathrm{AmineH}_3^{3+}$$

(where Amine = $\mathrm{Et_4dien}$, $\mathrm{Et_2dien}$, $\mathrm{Me_4dien}$).

By selecting reactions in which the tridentate ligand was directly replaced, ligand unwrapping would be forced to occur.

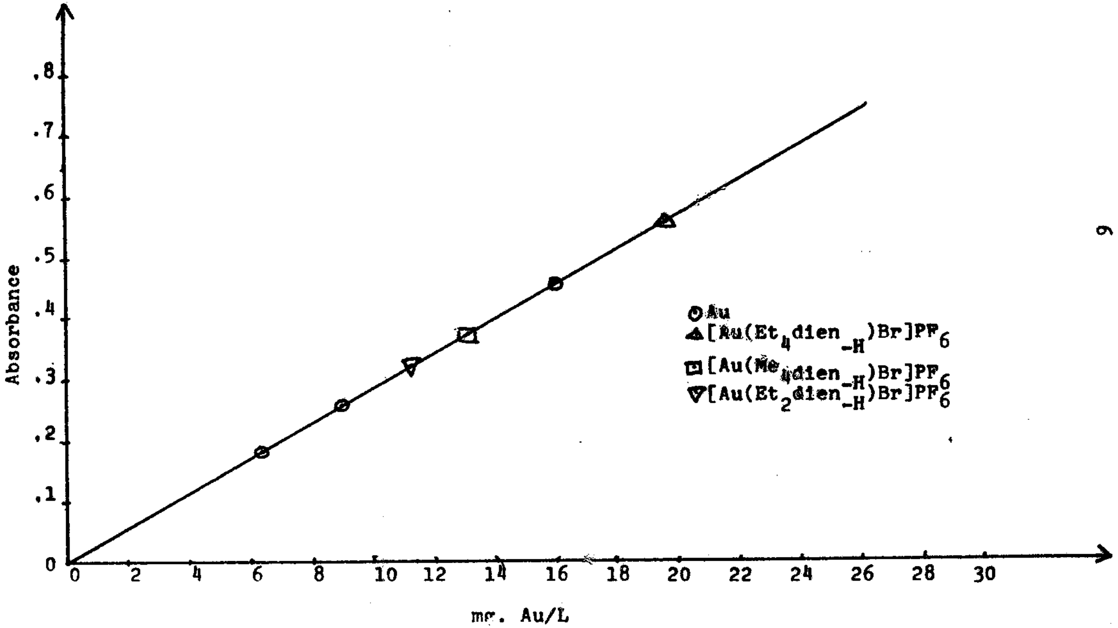
EXPERIMENTAL

Materials: Fine gold powder, purity better than 99.99%, and ammonium hexafluorophosphate were obtained from Alfa Inorganics, Inc. The Et_4dien, Me_4dien, and Et_2dien were obtained from Ames Laboratories, Inc. All other chemicals used were reagent grade.

Analyses: The complexes. which were prepared as the hexafluorophosphate salts, were analyzed for gold content by dissolving a small, accurately measured amount of the complex in aqua regia followed by repeated evaporation with concentrated HCl to remove all volatile nitrogen oxides. The solution was evaporated down three times to approximately one milliliter. The tetrachlorauric acid solutions thus obtained were diluted with 0.2 M $HClO_4$ to a concentration of 10^{-4} M. The absorbances of these solutions were measured at 314 nanometers using a Cary Recording Spectrophotometer Model 14MS. The concentration of the gold was then measured from a standard curve of absorbance vs. concentration of $HAuCl_4$ prepared using pure gold. (Figure 1)

FIGURE 1

Absorbance of $AuCl_4^-$ vs. Au Concentration at 314 nm



Preparation of Complexes: $HAuBr_4$ was prepared by dissolving 0.5 g of gold metal in 2 ml of HNO_3, then adding 10 ml of HBr. The solution then was evaporated repeatedly with HBr. On the third evaporation, the volume was reduced to 2-3 ml; and upon cooling, $HAuBr_4$ solidified.

$[Au(Et_4dien_{-H})Br]PF_6$: The $HAuBr_4$ crystals were then dissolved in 20 ml of cold distilled H_2O at less than 5° C. Seven ml of Et_4dien were added to 80 ml of distilled water and maintained at 0° C, while stirring with the use of a Stir Kool, Model SK 12, manufactured by Thermoelectrics Unlimited, Inc. The $HAuBr_4$ solution was added dropwise, a purplish red solution being formed. HBr was added dropwise to a pH value of 6. The pH was measured with a Fischer Accumet pH meter, calibrated with Beckmann pH 6.86 Buffer. At a pH of ca. 10, a purple precipitate formed. As additional HBr was added, the precipitate dissolved again. The resulting deep red solution, still at less than 5° C was filtered to remove reduced gold. One gm of NH_4PF_6 was then added to the filtrate. At 0° C, the formation of the precipitate did not occur. The solution was then quickly frozen with liquid N_2, and another gram of NH_4PF_6 was then sprinkled on top of the frozen solution. The solution was then thawed with vigorous agitation with cold H_2O and a brownish-red precipitate formed. The final product was collected on filter paper, washed with ether and dried in a desiccator containing $CaCl_2$. The product was stored under refrigeration. A yield of 25.4% (based on the weight of gold) was obtained.

Analysis: Calculated for $[Au(Et_4dien_{-H})Br]PF_6$: Au 31.0%; Found: Au 31.4%.

$[AuEt_2dien_{-H})Br]PF_6$: The procedure used for the synthesis of $[Au(Et_2dien_{-H})Br]PF_6$ was similar to that employed for $[AuEt_4dien_{-H})Br]PF_6$ with a few exceptions. Upon addition of $HAuBr_4$ to the aqueous solutions, a red oil formed. The oil similarly dissolved at pH of 6. The freeze-thaw method did not directly yield the precipitate. Instead, the solution was refrozen to form a bright yellow solid. One gram of NH_4PF_6 was sprinkled on top of the solid. The solid was then Roto-sublimated on a Buchler Instruments Flash Evaporator, Model No. PF-10DN. When the solution's volume was reduced to half its original volume, orange crystals were observed to form. The volume was reduced to 5 ml and the resultant bright orange-yellow crystals were collected on filter paper, and washed with ether. The product was then dried in a desiccator with $CaCl_2$ and also stored in a refrigerator. The yield was 41.2% based on the weight of gold.

Analysis: Calculated for $[AuEt_2dien_{-H})Br]PF_6$: Au 33.9%; Found: Au 33.9%.

$[Au(Me_4dien_{-H})Br]PF_6$: The procedure used for the synthesis of this complex was virtually the same as that used for the synthesis of $[AuEt_4dien_{-H})Br]PF_6$. However, the precipitate formed after freeze-thawing had to be recrystallized for purification. The precipitate was first dissolved in 2 ml of acetone and then 100 ml of distilled H_2O was added. This solution then was Roto-evaporated with the flash evaporator previously mentioned. Bright red-brown crystals were formed, very similar in appearance to the $[Au(Et_4dien_{-H})Br]PF_6$ crystals. The yield was 40.5% based on the weight of gold.

Analysis: Calculated for $[Au(Me_4dien_{-H})Br]PF_6$: Au 33.9% Found: Au 33.8%.

KINETIC STUDIES

Earlier studies of the aqueous solution chemistry of Au(III) with a variety of diens indicated that: (a) the conjugate base 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 undergo decomposition in hydrohalic acids: (d) the conjugate acids of these complexes are stable in $HClO_4$.[14,15,16]

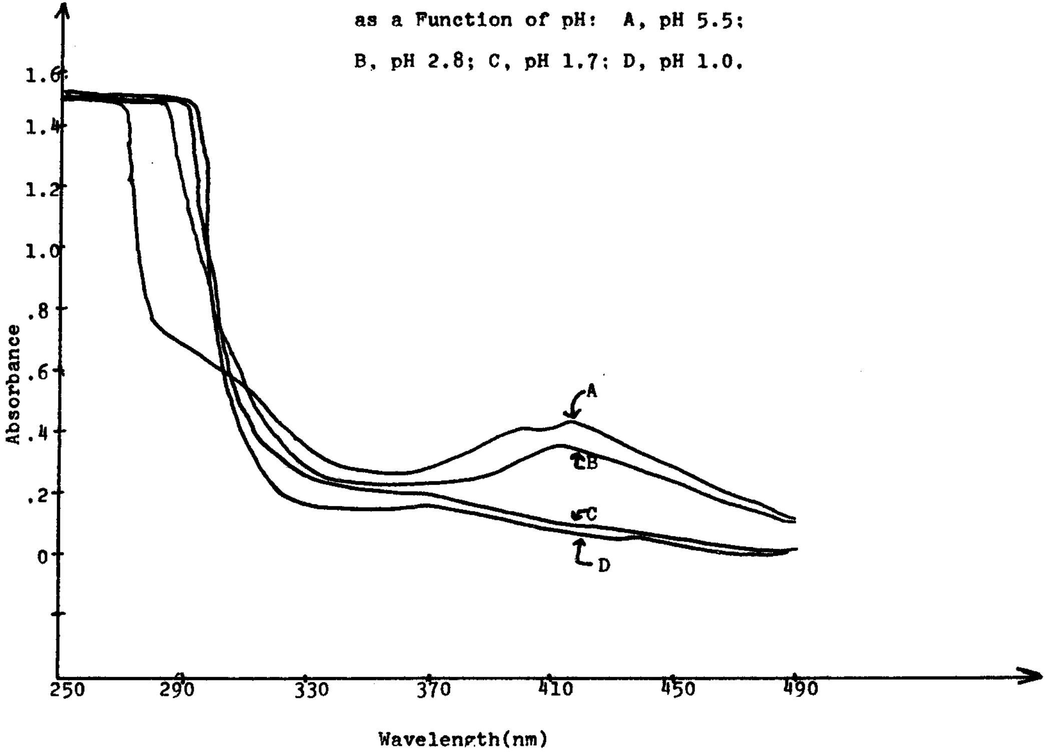
Since $[Au(Et_4dien_{-H})Br]^+$, $[Au(Me_4dien_{-H})Br]^+$, and $[Au(Et_2dien_{-H})Br]^+$ all exist as Au(III) dien complexes, one must find the optimal pH at which $HClO_4$ converts these ions to their conjugate acid complexes and represses the hydrolysis of the complexes. Also a suitable wavelength had to be determined to optimize the difference in absorbance of reactant relative to product. In the hope of finding uniform conditions for all three complexes, these parameters were determined for the $[Au(Et_4dien_{-H})Br]^+$ ion and used for the other complexes as well. Due to the similarity of these complexes, the uniform conditions would make later comparisons of results less complicated.

The optimal pH for the kinetic study was determined by dissolving enough $[Au(Et_4dien_{-H})Br]PF_6$ in 100 ml of distilled H_2O to make a 2.6×10^{-4} M solution of $[Au(Et_4dien_{-H})Br]^+$. The absorbance of this solution without any acid or base present was studied with a Perkin-Elmer Model 202 Spectrophotometer over a wavelength range of 250 to 500 nm. This Solution A (See Figure 2) had a pH of ca. 5.5. Solution A showed a distinct peak at 415 nm which was thought to be indicative of the hydrolysis product, $[Au(Et_4dien_{-H})OH]^+$. Solutions B, C, D were obtained by adding increments of $HClO_4$ to yield pHs of 2.8, 1.7, and 1.0, respectively. The pHs of these solutions were determined with a Fischer Accumet pH meter which was calibrated with Beckmann pH 6.86 and pH 4.01 buffers. The hydrolysis is repressed completely at pH of 1.0 and the complex exists in its acid form. A pH of ca. 1 with $HClO_4$ was determined to be the optimal pH for the kinetic study.

The optimal wavelength for the kinetic study was determined at 25° C by comparing the absorption spectrum of $[Au(Et_4dien)Br]^{2+}$, the reactant, with the spectrum of the product, $AuBr_4^-$, over a wavelength range of 250 to 500 nm. A solution of 0.10 M bromide was made up in 0.30 M $NaClO_4$ and allowed to react with 5.2×10^{-4} M $[Au(Et_4dien)Br]^{2+}$ in 0.20 M $HClO_4$. One ml of the bromide solution and one ml of the complex solution were simultaneously added into a quartz cell and the spectrum recorded. After mixing, an ionic strength of 0.30, a pH of ca. 1, and a final bromide concentration of .05 M existed. The system was maintained at $25.0 \pm 0.1^\circ$ C by placing the solutions and the quartz cells

FIGURE 2

Absorption Spectra of $[Au(Et_4dien_{-H})Br]^+$ as a Function of pH: A, pH 5.5; B, pH 2.8; C, pH 1.7; D, pH 1.0.



in contact with a circulating P.M. Tamson constant temperature bath. Figure 3 reveals that upon completion of the reaction. $AuBr_4^-$ absorbs strongly at 380 nm (Curve A). In comparison, the $[Au(Et_4dien)Br]^{2+}$ ion does not absorb at 380 nm (Curve B). 380 nm was selected as the optimal wavelength for the kinetic studies.

The reactions under study in this paper were:

(1) $[Au(Et_4dien)Br]^{2+} + 3Br^- \longrightarrow AuBr_4^- + Et_4dien$

(2) $[Au(Me_4dien)Br]^{2+} + 3Br^- \longrightarrow AuBr_4^- + Me_4dien$

(3) $[Au(Et_2dien)Br]^{2+} + 3Br^- \longrightarrow AuBr_4^- + Et_2dien$

The procedure used for the kinetic study of these reactions was uniform for all kinetic runs in every case. The complexes were dissolved in one ml of acetone and then diluted to 0.20 M $HClO_4$. The concentration of complex ranged from 2 x 10^{-4} M to 3 x 10^{-4} M. The kinetic runs were studied using bromide concentrations in the range 0.01 M to 0.20 M. The bromide solutions were prepared by dissolving exact amounts of NaBr and $NaClO_4$ to produce, after mixing, a total ionic strength of NaBr and $NaClO_4$ of 0.40. Since this solution was then mixed with an equal volume of 0.20 M $HClO_4$, reactions under study all had total ionic strengths of 0.30. Rates were determined at 25.0 ± 0.1° C using an Aminco-Morrow Stopped flow apparatus in conjunction with a Beckmann DU spectrophotometer. A constant temperature was maintained with a Temptrol 153 water bath from Precision Scientific Company that pumped H_2O through the mixing compartment of the

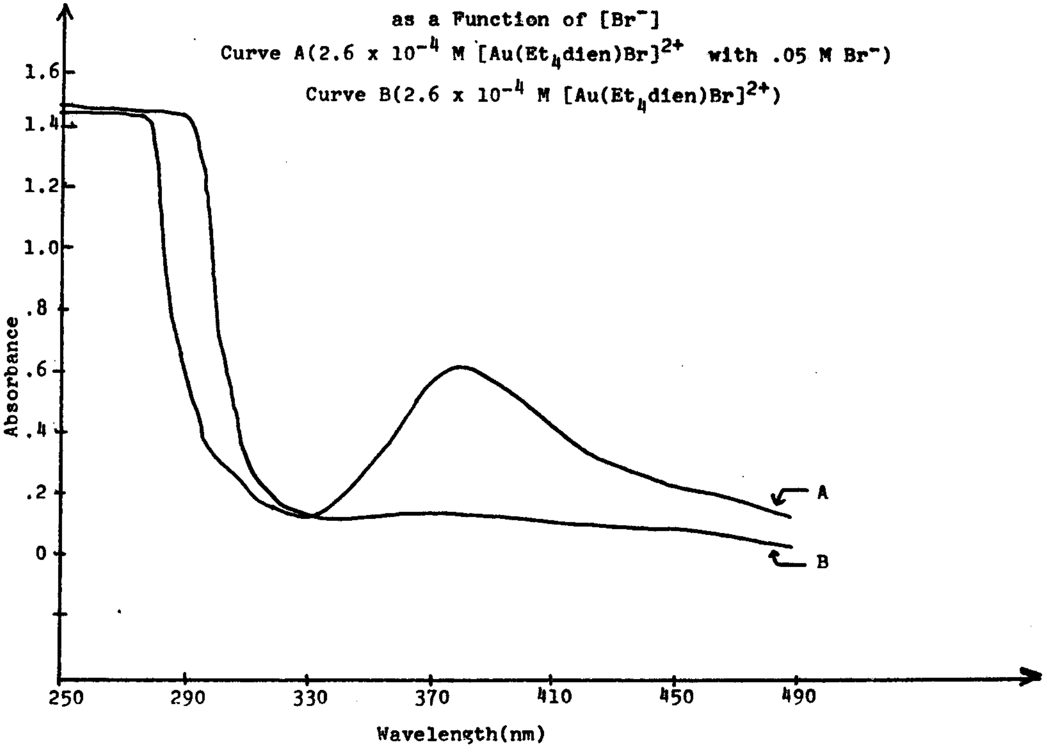
FIGURE 3

Absorption Spectra of $[Au(Et_4dien)Br]^{2+}$

as a Function of $[Br^-]$

Curve A(2.6×10^{-4} M $[Au(Et_4dien)Br]^{2+}$ with .05 M Br^-)

Curve B(2.6×10^{-4} M $[Au(Et_4dien)Br]^{2+}$)



Stopped-flow. (The output from the spectrophotometer was fed through an Aminco High Performance Kinetic Photometer into the vertical input of a Tektronix T912 Oscilloscope. Calibration was effected by setting a closed shutter zero transmittance and then setting 5 volt output on the oscilloscope to match 100% transmittance.) The reaction rates were now ready to be observed as percent change in transmittance in the stored traces of the oscilloscope. Each kinetic run called for a re-setting of the 0 and 100% transmittance values, to prevent instrument drift. Figure 4 shows a typical scan. For each complex, replicate runs were performed at each concentration level. Reproductibility was better than 1% transmittance.

The percent transmittance values were converted to absorbance values. The difference in absorbance at time "t" (A_t) and at the reaction's completion (A_∞) was obtained and the log of the difference plotted vs. time. From this plot, a linear curve produced a pseudo-first order rate constant, k_{obs}. which was calculated for every run. Plots of replicate runs yielded slopes which agreed within 10%. A typical curve for each complex is shown in Figures 5, 6, 7 for a bromide concentration of .01 M.

FIGURE 4

A Typical Scan for the Reaction of $[Au(Et_4dien)Br]^{2+}$ with 0.01 M NaBr, Followed as a Decrease in Transmittance with Time at 380 nm. Concentration of Complex is 2.0×10^{-4} M

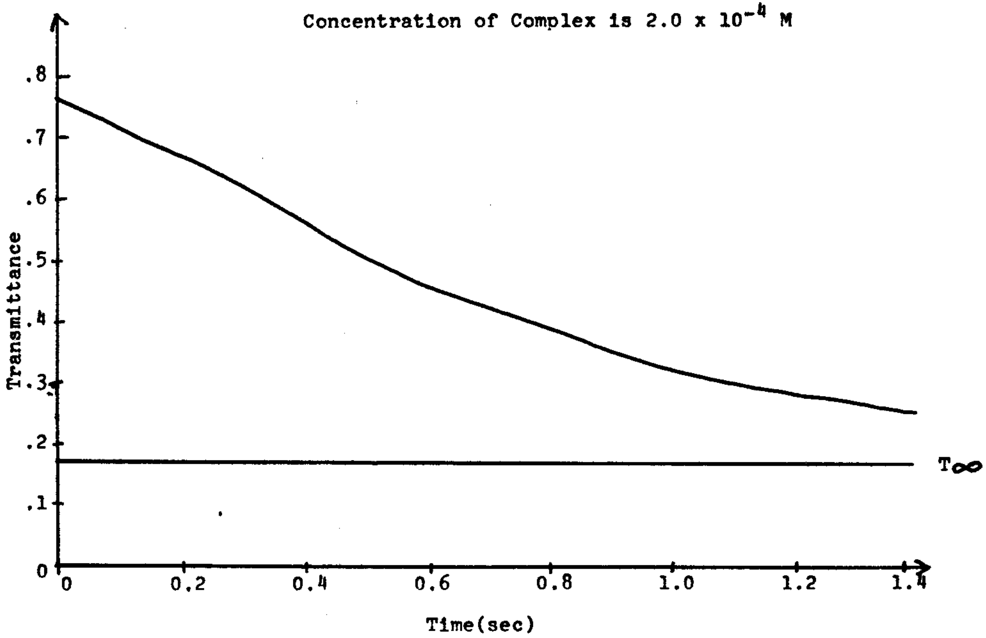


FIGURE 5

Graph of $-\log(A_{\infty}-A_t)$ vs. Time for the Reaction of $[Au(Et_4dien)Br]^{2+}$ with 0.01 M Br^-

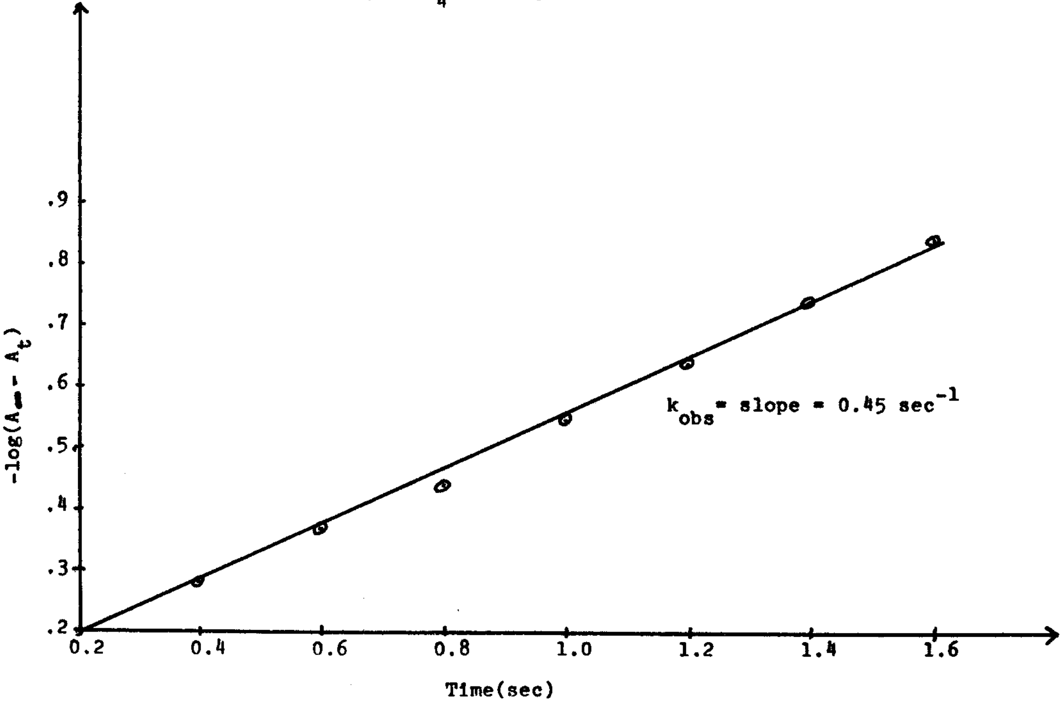
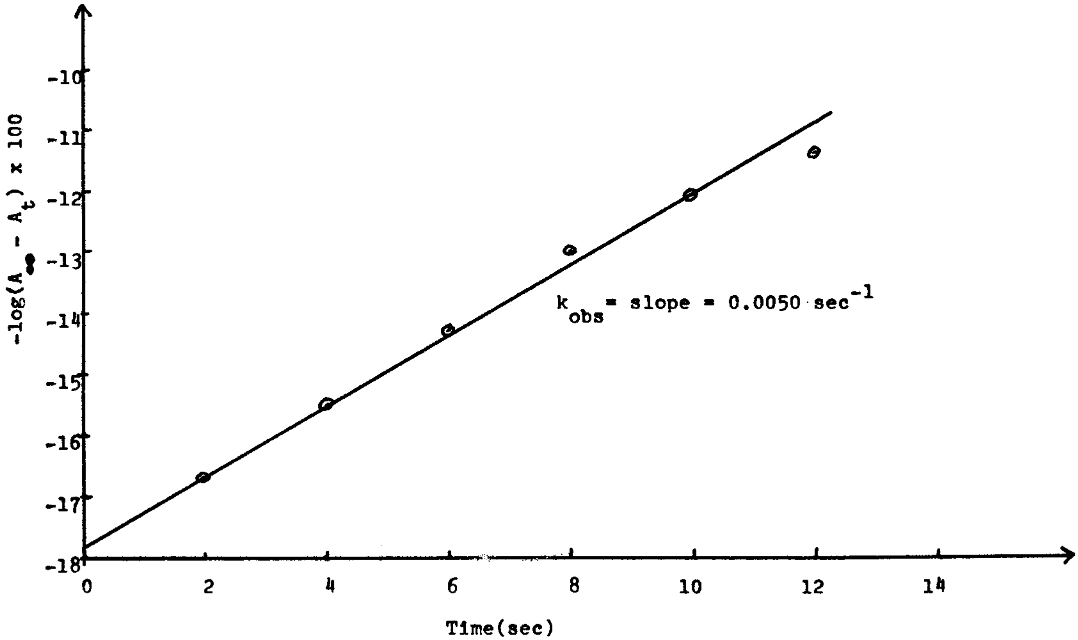

k_{obs} = slope = 0.45 sec^{-1}

FIGURE 6

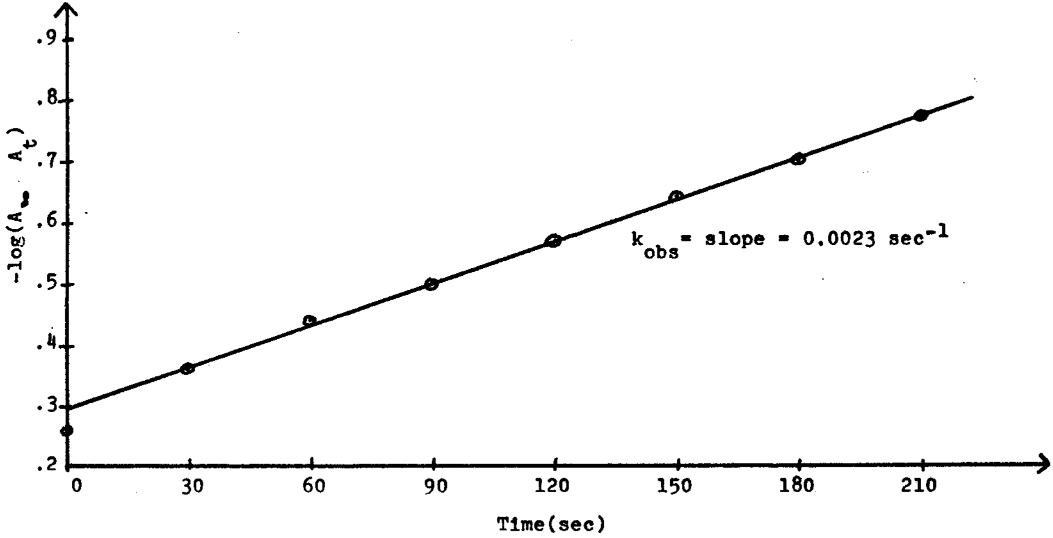
Graph of $-\log(A_\infty - A_t)$ vs. Time for the Reaction of $[Au(Me_4dien)Br]^{2+}$ with 0.01 M Br^-



k_{obs} = slope = 0.0050 sec^{-1}

FIGURE 7

Graph of $-\log(A_\infty - A_t)$ vs. Time for the Reaction of $[Au(Et_2dien)Br]^{2+}$ with 0.01 M Br^-



k_{obs} = slope = 0.0023 sec^{-1}

RESULTS AND DISCUSSION

The pseudo first order rate constants (k_{obs}) obtained for the reactions:

$$[Au(amine)Br]^{2+} + 3Br^- \longrightarrow AuBr_4^- + amineH_3^{3+}$$

(where amine = Et_4dien, Et_2dien, Me_4dien) are given in Table 1. The values of k_{obs} are reproducible within 10% and are the average of several runs.

A possible general mechanism for chelate ligand unwrapping of Au(III) dien complexes is shown in Figure 8. In the first step, the terminal nitrogen of $[Au(amine)Br]^{2+}$, or R, unwraps and relieves the steric hindrance preventing bromide attack. This first intermediate, P_1, can either reattach and displace the bromide or it can be forced to further unwrap, in step (2), to form a second intermediate, P_2. P_2 then will either reattach or the ligand will completely unwrap and form the product, P, the tetrabromoaurate ion.

The overall rate law for this reaction mechanism is (See Appendix for derivation):

$$Rate = \frac{d[P]}{dt} = \frac{k_1k_2k_3[Br^-]^3[H^+][R]}{k_{-1}k_{-2}+k_{-1}k_3[Br^-]+k_2k_3[Br^-]^2}$$

Therefore, under the pseudo first order conditions used in this study:

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}k_{-2}+k_{-1}k_3[Br^-]+k_2k_3[Br^-]^2}$$

TABLE I

Pseudo First Order Rate Constants for:

$[Au(amine)Br]^{2+} + 3Br^{-} \longrightarrow AuBr_4^{-} + amineH_3^{3+}$

$\mu = 0.30$, $T = 25.0 \pm 0.1°C$ $[H^+] = 0.1$ M $HClO_4$

	k_{obs}(Sec^{-1})		
$[Br^-]$(M)	amine = Et_4dien [Complex]=$2.7x10^{-4}$M	amine = Me_4dien [Complex)=$2.8x10^{-4}$M	amine = Et_2dien [Complex]=$2.9x10^{-4}$M
.01	0.42	.0049	.0020
.02	0.69	.032	.0099
.03	1.3	.075	.027
.04	1.8	.16	.053
.05	2.3	.25	.062
.06	2.7	.35	.071
.07	3.4	.59	.091
.08	4.6	.75	.12
.09	5.5	.87	.13
.10	4.3	1.1	.16
.12	5.2	1.5	.20
.14	6.6	1.8	.23
.16	7.6	2.1	.26
.18	9.1	2.9	.36
.20	11.4	3.5	.43

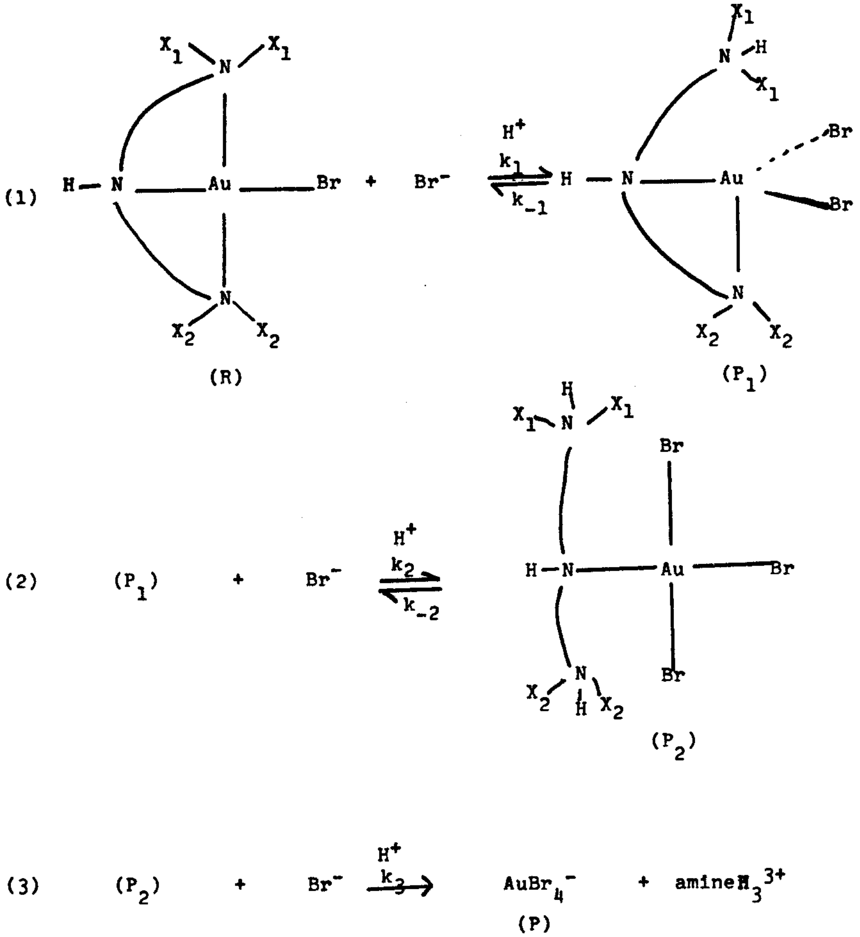


FIGURE 8. Overall reaction mechanism proposed for the following reactions:

$[Au(amine)Br]^{2+} + 3Br^- \longrightarrow AuBr_4^- + amineH_3^{3+}$

(where amine = Et_4dien, Et_2dien, Me_4dien)

At the lower concentrations of bromide, it can be assumed that $k_2k_3[Br^-]^2$ is negligible:

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}(k_{-2}+k_3[Br^-])}$$

At these concentrations, the order with respect to bromide ion is dependent on the relative magnitudes of k_{-2} and $k_3[Br^-]$. If reattachment at the terminal nitrogen of the second intermediate, P_2, is more important than formation of the product, then $k_{-2} \gg k_3[Br^-]$:

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}k_{-2}}$$

Thus, this assumption predicts a third order dependence on $[Br^-]$. On the other hand, if product formation is more important than reattachment of a terminal nitrogen of P_2, then $k_3[Br^-] \gg k_{-2}$:

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}k_3[Br^-]} = \frac{k_1k_2}{k_{-1}}[Br^-]^2[H^+]$$

At high bromide concentrations, $k_{-1}k_{-2}$ becomes negligible due to the difficulty of reattachment of the dangling end in excess bromide:

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}k_3[Br^-]+k_2k_3[Br^-]^2} = \frac{k_1k_2[Br^-]^2[H^+]}{k_{-1}+k_2[Br^-]}$$

The order with respect to bromide ion is dependent on the relative magnitudes of k_{-1} and $k_2[Br^-]$. If reattachment at the terminal nitrogen site of the first intermediate, P_1, is more important than the formation of P_2, then $k_{-1} \gg k_2[Br^-]$:

$$k_{obs} = \frac{k_1k_2}{k_{-1}} [Br^-]^2[H^+]$$

Or, second order dependence on bromide ion if reattachment is favored. If the formation of P_2 is more important than the reattachment process, then $k_2[Br^-] \gg k_{-1}$:

$$k_{obs} = \frac{k_1k_2[Br^-]^2[H^+]}{k_2[Br^-]} = k_1[Br^-][H^+]$$

A linear curve for a plot of k_{obs} vs. $[Br^-]$ indicates first order dependence on the concentration of bromide, with a slope of $k_1[H^+]$. A linear curve for a plot of k_{obs} vs. $[Br^-]^2$ indicates a second order dependence on bromide, with a slope of $(k_1k_2/k_{-1})[H^+]$. Another plot that will yield the order of dependence on $[Br^-]$ is log (k_{obs}) vs. log $([Br^-])$. The slope will equal the order of bromide dependence in this case. This plot is more sensitive to changes in slope and proved very useful in these studies.

Figure 9 shows a plot of log (k_{obs}) vs. log $([Br^-])$ for the reaction of $[Au(Et_4dien)Br]^{2+}$. The graph yields a slope of 1.1 and a correlation coefficient of 0.992 for all points on the curve. If one excludes the points corresponding to 0.08 M and 0.09 M Br^-, one again gets a slope of 1.1 and a correlation coefficient of 0.997. This plot denotes a first order dependence on $[Br^-]$ for $[Au(Et_4dien)Br]^{2+}$. In

FIGURE 9

The log of k_{obs} vs. the log ([Br^-])
for $[Au(Et_4dien)Br]^{2+}$

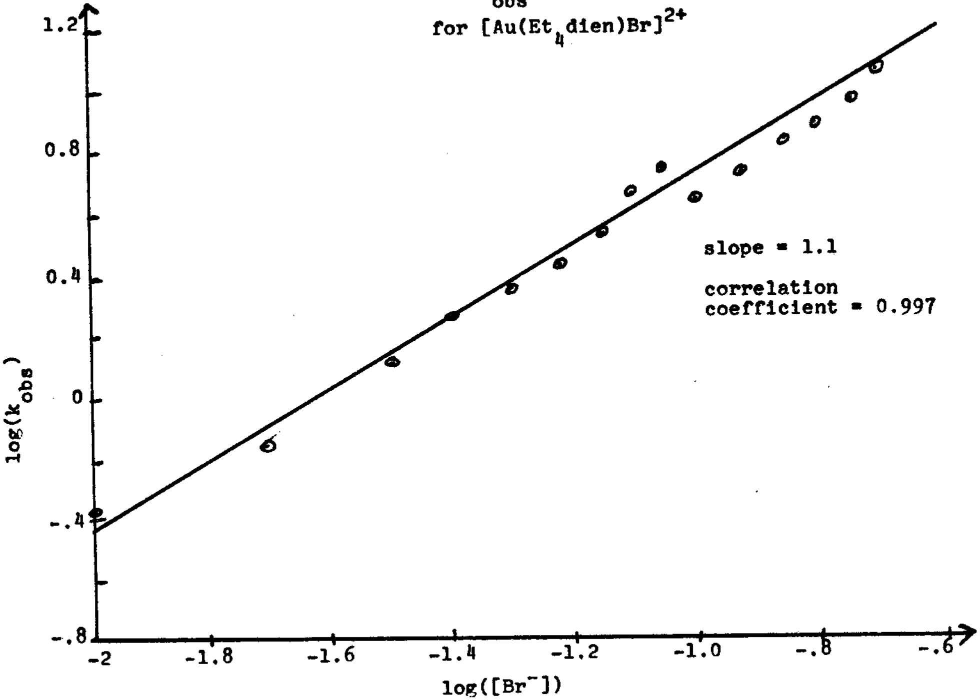


Figure 10, a plot of k_{obs} vs. [Br^-] reveals a linear curve as well. Assuming again that the values corresponding to 0.08 and 0.09 M are relatively high and excluding them, one finds a slope of 53 and a y-intercept of -0.46. The correlation coefficient is 0.989. Therefore, k_1 is 530 l-sec/mole ($k_1[H^+] = 0.1k_1 = 53$). A negative y-intercept is impossible based only on first order with respect to bromide. Apparently, at concentrations of bromide approaching zero, second and third order dependence on bromide must occur. This explanation correlates with the second and third order rate laws for low [Br^-].

First order dependence on bromide indicates that P_1 apparently does not reattach appreciably over a range of 0.01 M to 0.20 M Br^-. Rather, further substitution is favored to form $AuBr_4^-$. The rate determining step for this reaction is step (1) of the reaction mechanism in Figure 8:

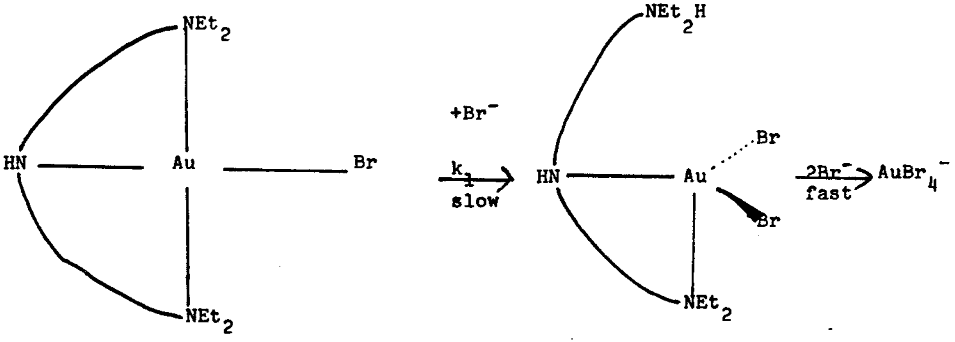
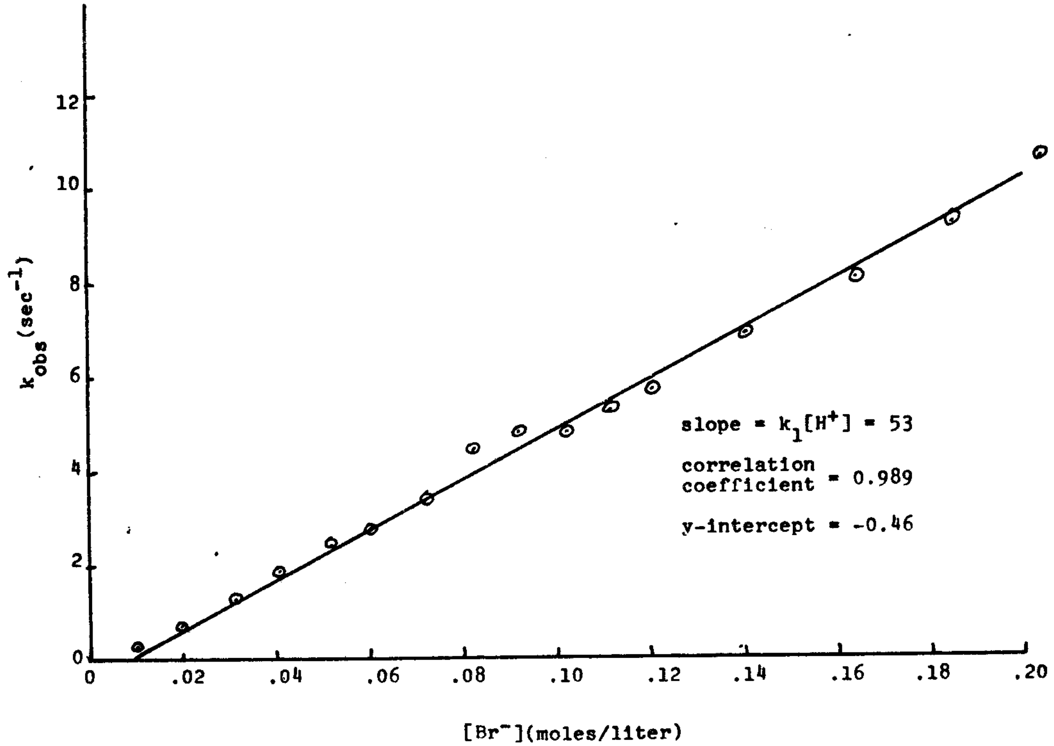


FIGURE 10

Observed Rate Constant for $[Au(Et_4dien)Br]^{2+}$

vs. $[Br^-]$ at T = 25.0° C



The occurrence of reattachment is negligible over these $[Br^-]$ ranges which exemplifies the instability of the tridentate $[Au(Et_4dien)Br]^{2+}$ relative to the bidentate P_1, $[Au(Et_4dien)Br_2]^+$. Apparently, the presence of the bulky ethyl groups seriously hinders reattachment at the dangling terminal nitrogen site. Since this first order dependence is observed over almost the entire range of $[Br^-]$, attack by the second bromide becomes favored over reattachment of the chelate at very low bromide concentrations.

Figure 11 shows a plot of log (k_{obs}) vs. log ($[Br^-]$) for $[Au(Me_4dien)Br]^{2+}$. The graph yields a slope of 2.1 and a correlation coefficient of 0.995 (Curve A). The point corresponding to 0.01 M Br^- can be omitted if one assumes that at this low bromide concentration the order of dependence may be increasing. With this omission, one obtains a slope of 2.0 and a correlation coefficient of 0.995. (Curve B) The plot indicates second order dependence on bromide for $[Au(Me_4dien)Br]^{2+}$. Therefore,

$$\text{Rate} = \frac{k_1k_2}{k_{-1}}[Br^-]^2[H^+][R]$$

and

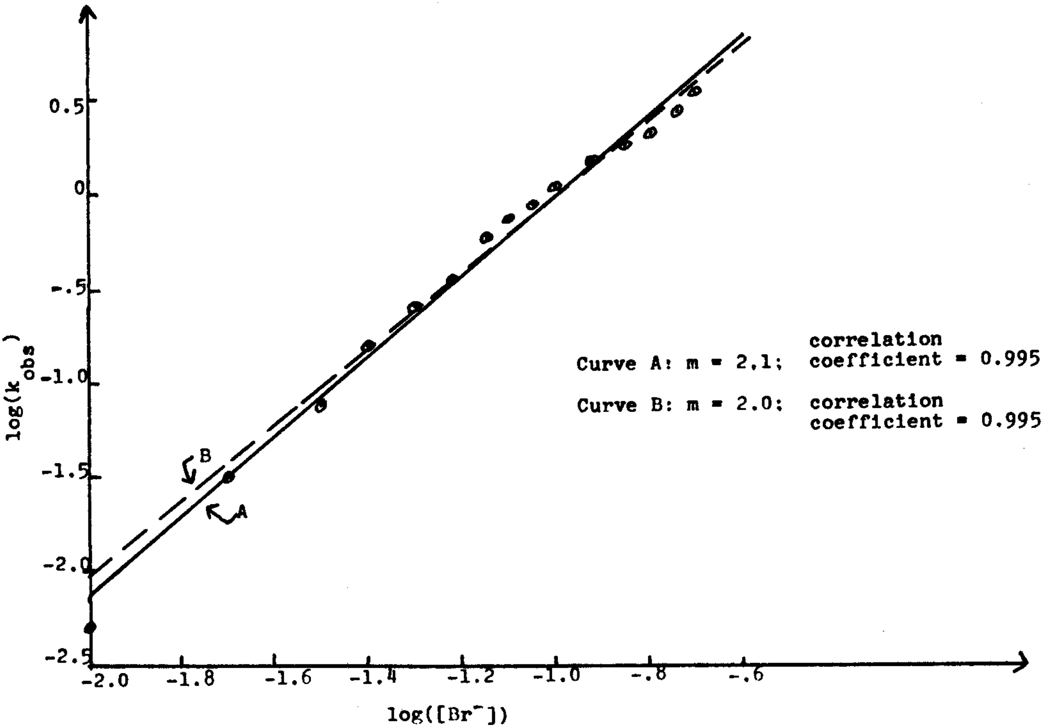
$$k_{obs} = \frac{k_1k_2}{k_{-1}}[H^+][Br^-]^2$$

A plot of k_{obs} __vs.__ $[Br^-]^2$ should yield a linear curve

FIGURE 11

The log of k_{obs} *vs.* the log ($[Br^-]$)

for $[Au(Me_4dien)Br]^{2+}$



with a slope of $(k_1k_2/k_{-1})[H^+]$. Figure 12 shows this plot. Curve A shows the plot inclusive of all points. For this curve, one finds a slope of 92 and a correlation coefficient of 0.973. Curve A has a rather low correlation coefficient. Curve B excludes the point corresponding to 0.01 M Br^-. For this curve, one obtains a slope of 86 and a correlation coefficient of 0.995! Apparently, exclusion of this point is justified based on the increasing order of bromide at very low concentrations.

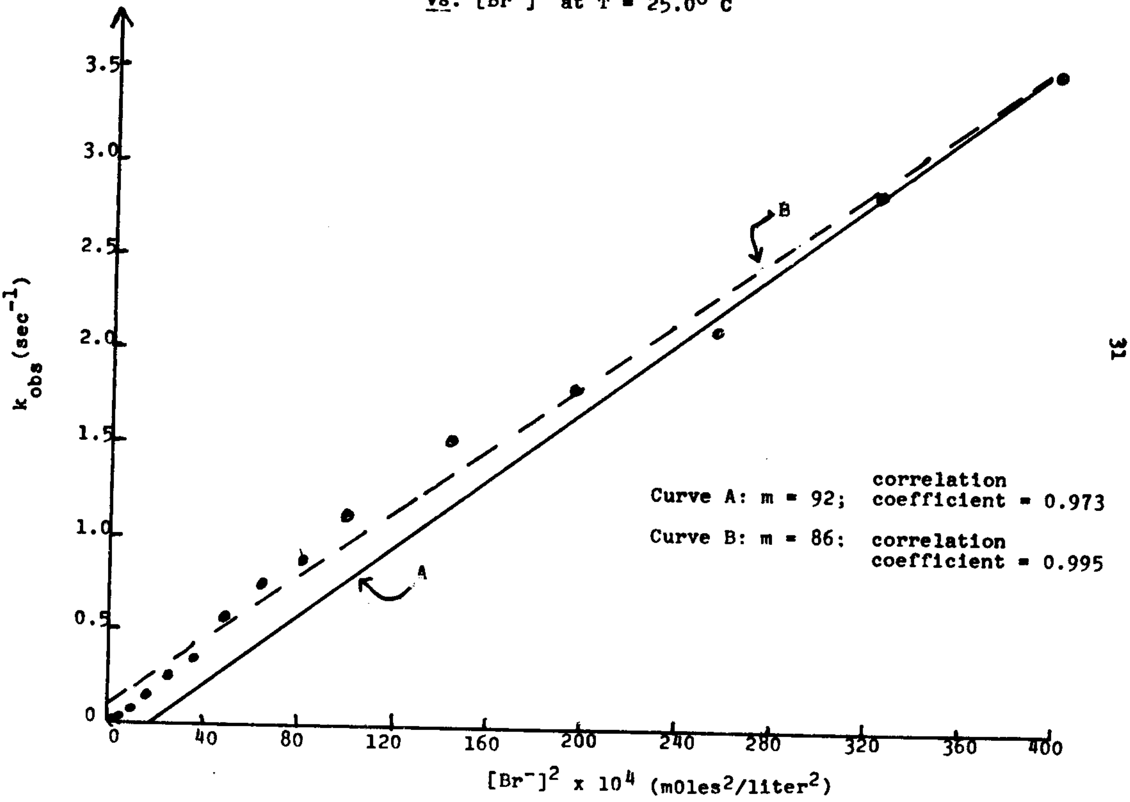
If a second order dependence on bromide is accepted for $[Au(Me_4dien)Br]^{2+}$, it is achieved by either assuming that reattachment of the terminal nitrogen site of P_1 is more important than the formation of P_2 $(k_{-1} >> k_2[Br^-])$ as argued for the high concentration of bromide case, or by assuming that reattachment at the terminal nitrogen site of P_2 is more important than the formation of P as in the low bromide concentration case $(k_{-2} >> k_3[Br^-])$. One would predict, however, that the second order dependence is due to the reattachment at the terminal nitrogen site of P_1. This prediction is substantiated by the stability of Me_4dien over Et_4dien as a tridentate ligand. (Fant and Weick showed that $[Au(Et_4dien)Cl]^{2+}$ decomposed to $AuCl_4^-$ in 1 M HCl, whereas $[Au(Me_4dien)Cl]^{2+}$ does not decompose.[17])

Whereas $[Au(Et_4dien)Br]^{2+}$ has little tendency for reattachment to form P_1 and is therefore first order in

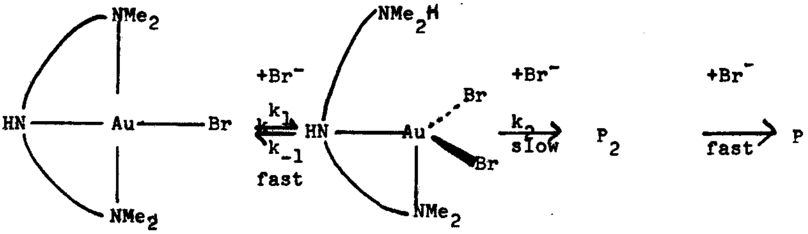
FIGURE 12

Observed Rate Constant for $[Au(Me_4dien)Br]^{2+}$

vs. $[Br^-]^2$ at T = 25.0° C



bromide, $[Au(Me_4dien)Br]^{2+}$ shows significant tendency for reattachment to form P_1 and is second order in bromide:



In the case of $[Au(Me_4dien)Br]^{2+}$, N– bond reattachment dominates its kinetics. P_1 faces a competition between making a bond with the terminal nitrogen again (k_{-1}) or breaking the terminal Au-N bond and making a new bond with the second attacking bromide (k_2). The key difference between $[Au(Me_4dien)Br]^{2+}$ and $[Au(Et_4dien)Br]^{2+}$ is the size of the alkyl group on the detached nitrogen. Thus the difference in kinetic order can be traced to the influence of the larger ethyl groups in hindering reattachment at the dangling terminal nitrogen.

Figure 13 shows the plot of k_{obs} vs. $[Br^-]^2$ for $[Au(Et_2dien)Br]^{2+}$. The plot, however, does not yield a consistent straight line over the entire range of bromide concentration. It suggests that a change in the order with respect to bromide is occurring.

Figure 14 is a much more revealing plot. This graph shows the plot of $\log(k_{obs})$ vs. $\log([Br^-])$. Curve A, using all the points on the curve, has a slope of 1.7 with a correlation coefficient of 0.991. A glance at the points plotted indicates that the slope is decreasing with increasing bromide concentration. Curve B results when only the points from 0.01 M to 0.05 M bromide are used. A slope of 2.1 and a correlation coefficient of 0.998 are obtained. So, k_{-1} is much greater than $k_2[Br^-]$ over the range of 0.01 M to 0.05 M bromide.

Curve C uses only the points from 0.06 M to 0.20 M bromide. In this curve, one obtains a slope of 1.4 and a correlation coefficient of 0.995. The reduction in slope is explained by $k_2[Br^-]$ becoming more important relative to k_{-1}:

$$k_{obs} = \frac{k_1k_2[Br^-]^2[H^+]}{k_{-1} + k_2[Br^-]}$$

As the concentration of bromide increases, $[Au(Et_2dien)Br]^{2+}$ moves from a second toward a first order dependence on bromide.

An examination of P_1 for each complex reveals the explanation for their subtle differences in kinetic behavior.

FIGURE 13

Observed Rate Constant for $[Au(Et_2dien)Br]^{2+}$

vs. $[Br^-]^2$ at T = 25.0° C

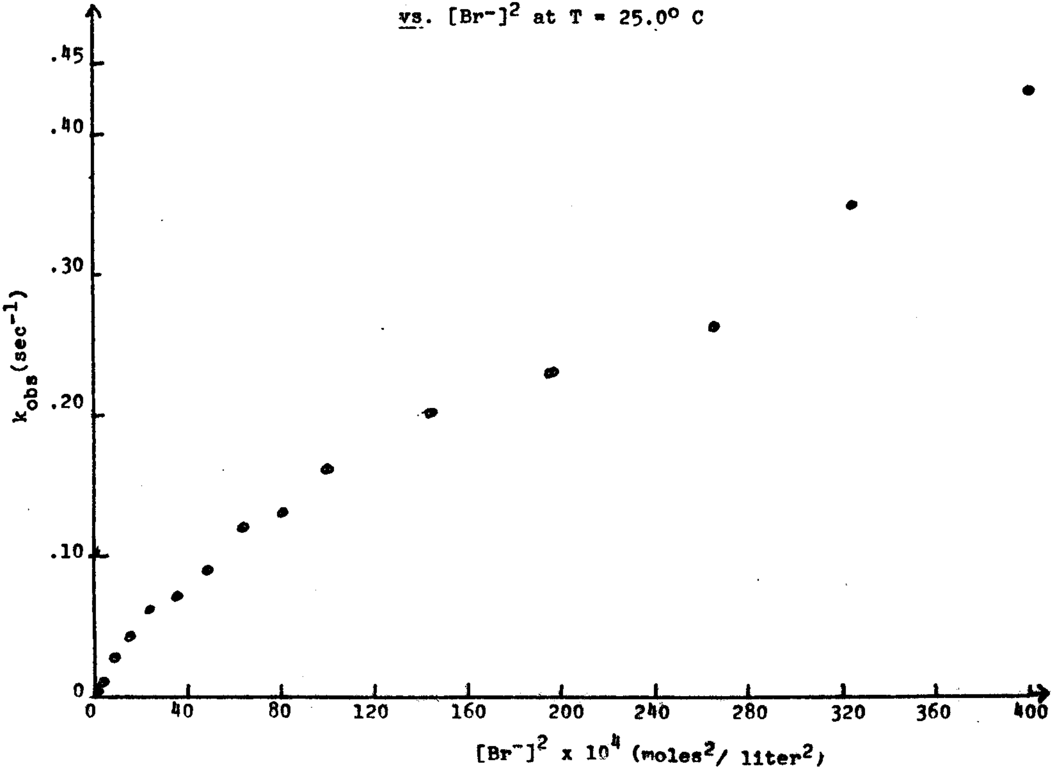
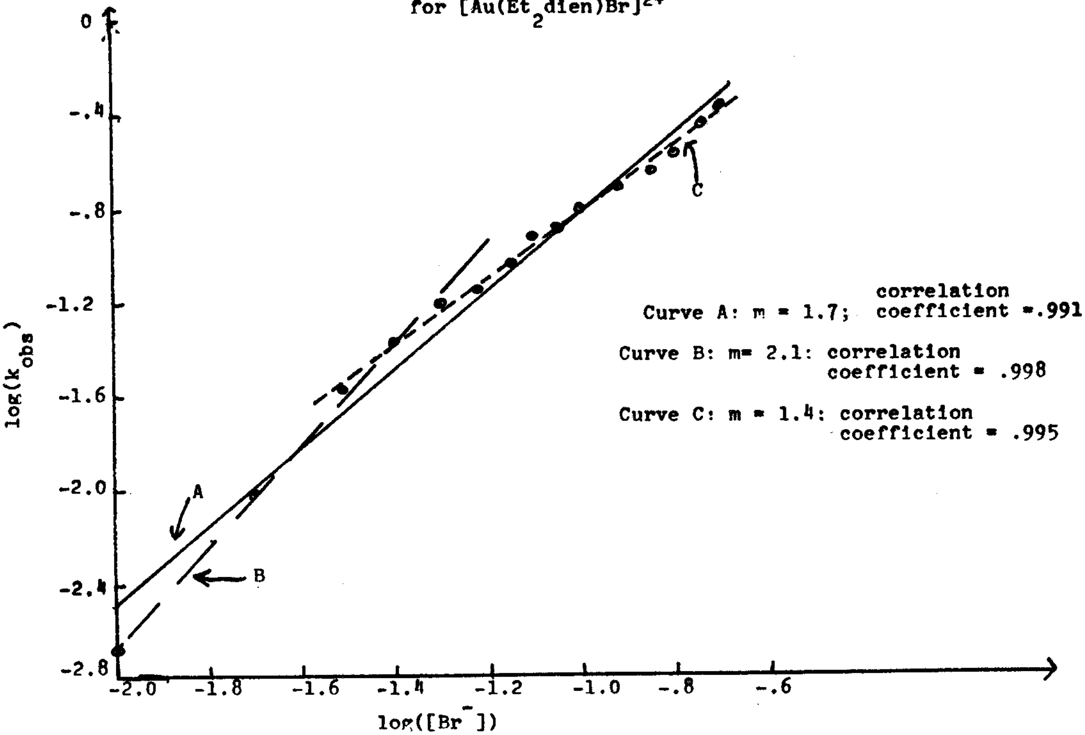
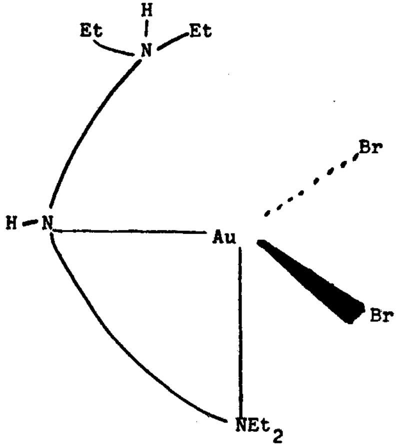


FIGURE 14

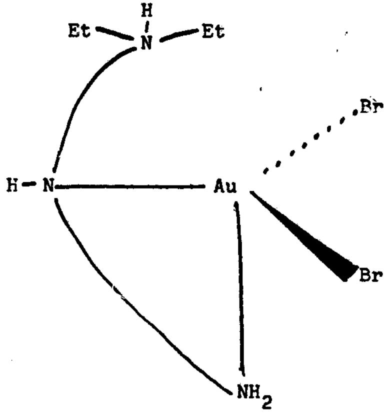
The log of k_{obs} vs. the log ($[Br^-]$) for $[Au(Et_2dien)Br]^{2+}$



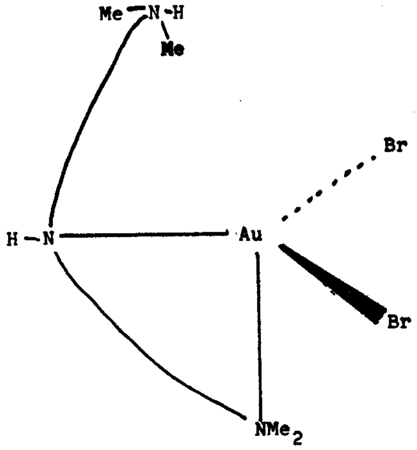
$[Au(Et_4dien_{+H})Br_2]^{2+}$ has virtually no reattachment ability due to steric hindrance of the bulky ethyl groups at the dangling terminal nitrogen:



The same argument can be extended to $[Au(Et_2dien_{+H})Br_2]^{2+}$:



$[Au(Me_4dien_{+H})Br_2]^{2+}$, on the other hand, has significant reattachment ability due to less steric hindrance provided by methyl groups at the dangling terminal nitrogen site:



Hence, the following order of magnitude of k_{-1} for P_1 of each complex is given:

$[Au(Me_4dien_{+H})Br_2]^{2+} \gg [Au(Et_4dien_{+H})Br_2]^{2+} \approx [Au(Et_2dien_{+H})Br_2]^{2+}$

The attack at the attached terminal nitrogen site by the second bromide is dependent on the relative strength of the Au-N bond. The term, $k_2[Br^-]$, will depend on the effect of the alkyl groups on the attached terminal nitrogen of P_1. Fant and Weick show that $[Au(Et_4dien)Cl]^{2+}$ breaks down to $AuCl_4^-$ in 1 M HCl whereas $[Au(Me_4dien)Cl]^{2+}$ does not.[18] They suggest that the ethyl groups weaken the Au-N bond and favor detachment of the terminal nitrogen. Based on this suggestion. the relative strength of the remaining terminal Au-N bond of P_1 can be assumed to be:

$$[Au(Et_4dien_{+H})Br_2]^{2+} \ll [Au(Me_4dien_{+H})Br_2]^{2+} \cong [Au(Et_2dien_{+H})Br_2]^{2+}$$

Since one is comparing k_{-1} and $k_2[Br^-]$ for the P_1 form of these three complexes, it is important to emphasize that the comparisons are relative for each complex. For $[Au(Et_4dien)Br]^{2+}$, $k_2[Br^-]$ is always more significant than k_{-1} because: (a) Ethyl groups on the protonated dangling terminal nitrogen site make reattachment unlikely (k_{-1} very small); (b) Ethyl groups on the attached terminal nitrogen site favor unwrapping to form P_2 ($k_2[Br^-]$ relatively large). So the P_1 structure for the complex can be expected to readily react to form P_2 giving first order kinetics over the entire Br^- concentration range.

For $[Au(Me_4dien)Br]^{2+}$ over the same Br^- concentration range, k_{-1} is always more significant than $k_2[Br^-]$. This appears to be because (a) Methyl groups on the protonated dangling terminal nitrogen site do not seriously hinder reattachment (k_{-1} relatively large); and (b) Methyl groups on the attached terminal nitrogen site do not favor unwrapping to form P_2 ($k_2[Br^-]$ relatively small). Thus second order kinetics are observed over the Br^- concentration range.

For $[Au(Et_2dien)Br]^{2+}$, k_{-1} is more significant at low concentrations of bromide than $k_2[Br^-]$ because: (a) As in

Et_4dien complex, the ethyl groups on the detached terminal nitrogen site of P_1 sterically hinder reattachment (k_{-1} relatively small); (b) the hydrogens on the attached terminal nitrogen site of P_1 do not favor unwrapping to form P_2 ($k_2[Br^-]$ relatively small). At low concentrations of bromide, k_{-1} is much greater than $k_2[Br^-]$ and second order dependence on bromide is observed. As concentration increases, $k_2[Br^-]$ becomes comparable to k_{-1} and the order decreases. This can occur over the range studied because k_{-1} is a relatively small value. However, a decrease in order is not observed for $[Au(Me_4dien)Br^-)^{2+}$ because k_{-1} is relatively large.

In conclusion, this paper has shown the importance of P_1 in the chelate ligand unwrapping reactions of $[Au(Et_4dien)Br]^{2+}$, $[Au(Et_2dien)Br]^{2+}$, $[Au(Me_4dien)Br]^{2+}$. The effect of the alkyl environment on each terminal nitrogen site has been invoked to explain the observed dependence on bromide. The subtle differences in the kinetic behavior of these complexes hinges on the competition between reattachment at one terminal nitrogen site in P_1 vs. detachment at the other attached terminal nitrogen site.

More extensive studies at concentrations of 0.001 M to 0.01 M bromide might reveal third order dependence on bromide. The mechanism of chelate ligand unwrapping is complex and requires study over a broad range of concentrations.

APPENDIX

Mathematical Derivation of Overall Rate Law:

The overall reactions studied:

$$[\mathrm{Au(amine)Br}]^{2+} + 3\mathrm{Br}^- \longrightarrow \mathrm{AuBr_4}^- + \mathrm{amineH_3}^{3+}$$

(where amine = Et_4dien, Et_2dien, Me_4dien).

The overall reaction mechanism proposed for these reactions is shown in Figure 8. The mathematical derivation of the overall rate law is shown sequentially. Based on Figure 8, R is $[\mathrm{Au(amine)Br}]^{2+}$, P_1 is the first intermediate formed with the dangling end, P_2 is the second intermediate in which only one nitrogen remains attached, and P is $\mathrm{AuBr_4}^-$. The derivation follows:

By Steady-State Approximations:

$$\frac{d[P_1]}{dt} \cong 0 = k_1[R][Br^-] - k_{-1}[P_1] + k_{-2}[P_2] - k_2[P_1][Br^-]$$

$$(1) \quad [P_1] = \frac{k_1[R][Br^-] + k_{-2}[P_2]}{k_{-1} + k_2[Br^-]}$$

$$\frac{d[P_2]}{dt} = 0 = k_2[P_1][Br^-] - k_{-2}[P_2] - k_3[P_2][Br^-]$$

$$(2) \quad [P_1] = \frac{k_{-2}[P_2] + k_3[P_2][Br^-]}{k_2[Br^-]}$$

Set (1) and (2) equal and solve for $[P_2]$:

$$[P_1] = \frac{k_1[R][Br^-] + k_{-2}[P_2]}{k_{-1} + k_2[Br^-]} = \frac{k_{-2}[P_2] + k_3[P_2][Br^-]}{k_2[Br^-]}$$

Therefore,

$$[P_2] = \frac{k_1k_2[R][Br^-]^2}{k_{-1}k_{-2} + k_{-1}k_3[Br^-] + k_2k_3[Br^-]^2}$$

Overall rate law;

$$\text{Rate} = \frac{d[P]}{dt} = k_3[P_2][Br^-][H^+]$$

Substitute expression for $[P_2]$:

$$\text{Rate} = \frac{k_1k_2k_3[Br^-]^3[H^+][R]}{k_{-1}k_{-2} + k_{-1}k_{-3}[Br^-] + k_2k_3[Br^-]^2}$$

$$\text{Rate} = k_{obs}[R]$$

$$k_{obs} = \frac{k_1k_2k_3[Br^-]^3[H^+]}{k_{-1}k_{-2} + k_{-1}k_{-3}[Br^-] + k_2k_3[Br^-]^2}$$

REFERENCES

1. William H. Baddley and Fred Basolo, Inorganic Chemistry, 3, 1087, (1964).
2. C. F. Weick and Fred Basolo, Inorganic Chemistry, 8, 576, (1966).
3, Fred Basolo and Ralph G. Pearson, "Mechanisms of Inorganic Reactions," Second Edition, John Wiley & Sons, Inc., New York, N.Y. (1967) p 379.
4. Ibid, p 376.
5. Ibid, p 377-8.
6. William H. Baddley and Fred Basolo, Journal of the American Chemical Society, 88:13, 2944, (1966).
7. Weick and Basolo, p 581.
8. John L. Burmeister and John C. Lim, Chemical Communication, 19, 1154, (1969).
9. David L. Fant and C. F. Weick, Inorganic Chemistry, 12, 1867, (1973).
10. J. S. Stevens, unpublished results.
11. Fant and Weick, p 1867.
12. J. W. Allison and R. S. Angelici, Inorganic Chemistry, 10, 2233, (1971).
13. T. S. Turan and D. B. Rorabacher, Inorganic Chemistry 11, 288, (1972).
14. W. H. Baddley, Fred Basolo, Harry B. Gray, Clarita Nölting, and A. J. Pöe, Inorganic Chemistry, 2, 923, (1963).

15. C. F. Weick, unpublished results.

16. Weick and Basolo, p 576.

17. Fant and Weick, p 1866.

18. Ibid.

BIBLIOGRAPHY

Baddley, William H., and Basolo, Fred. "A Kinetic Study of Substitution Reactions of Some Gold(III) Complexes." Inorganic Chemistry. 8, 1087, (1964).

Baddley, W. H., and Basolo, Fred. "Preparation and Kinetic Study of Some Sterically Hindered Palladium(II) Complexes." Journal of the American Chemical Society, 88·13, 2944 (1966).

Baddley. W. H., and Basolo, Fred. "The Importance of Steric Factors in Substitution Reactions of Metal Complexes. A Pseudo-octahedral Complex." Journal of the American Chemical Society, 86, 2075, (1964).

Baddley. W. H.. Basolo, Fred, et.al.. "Acidodiethylenetriaminegold(III) Complexes: Preparation, Solution Chemistry, and Electronic Structure." Inorganic Chemistry, 2, 921, (1963).

Basolo, Fred. and Pearson, Ralph G.. "Mechanisms of Inorganic Reactions." Second Edition, John Wiley and Sons, Inc.. New York, N.Y. (1967).

Burmeister. John L., and Lim, Fred C.. "Mechanistic Control by the Size of the Outgoing Group in a Palladium(II) Substitution Reaction." Chemical Communications, 19, 1154, (1969).

Goddard, John B., and Basolo Fred. "Rates and Mechanism of Substitution Reactions of Sterically Hindered Palladium(II) Complexes." Inorganic Chemistry, 7, 936. (1968).

Weick. C. F., and Basolo, Fred. "The Aqueous Solution Chemistry and Kinetic Behavior of a Pseudo-Octahedral Complex of Gold(III)." Inorganic Chemistry, 5. 576 (1966).

Weick, C. F. and Fant, D. L.. "Substitution Reactions of Sterically Hindered Gold(III) Complexes." Inorganic Chemistry. 12, 1867, (1973).

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