isomer. The tris(bipyridine)osmium(II) perchlorate obtained in this investigation showed a specific rotation of −1200° as compared to −3300° reported for the optically pure substance.

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A Kinetic Study of Substitution Reactions of Some Gold(III) Complexes

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Rate constants for the reactions of $[Au(dien)Cl]^{2+}$ (dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$) and/or its conjugate base, $[Au(dien\text{-}H)Cl]^+$ (dien-H = dien less a proton), with the reagents Br^-, I^-, SCN^-, N_3^-, and OH^- are reported. The results reported for the Au(III) systems are compared with data available for analogous Pt(II) complexes.

Introduction

Kinetic studies of substitution reactions of square-planar complexes are largely limited to the chemistry of platinum(II).[1] Other low-spin d^8 systems such as complexes of Pd(II), Ni(II), Au(III), Rh(I), and Ir(I) are also known to be square-planar. Investigations on these systems have not yet been extensive.

Analogous four-coordinated Au(III) and Pt(II) complexes are isoelectronic and isostructural. It is therefore of interest to compare the rates and mechanisms of substitution reactions of Au(III) with similar Pt(II) complexes. Rich and Taube[2] have investigated the exchange of chloride ion with $AuCl_4^-$. No other detailed study has been reported on exchange or substitution reactions of Au(III) complexes. This is in part because only a rather limited number of Au(III) complexes have been prepared and characterized and because of the ease with which these systems are reduced to Au(I) and Au.

The preparation and aqueous solution chemistry of complexes of the type $[Au(dien)X]^{2+}$ and $[Au(dien\text{-}H)X]^+$ was recently reported.[3] This paper reports the results of a kinetic investigation on the reactions of $[Au(dien)Cl]^{2+}$ and/or $[Au(dien\text{-}H)Cl]^+$ with the reagents Br^-, I^-, SCN^-, N_3^-, and OH^-.

Experimental

(A) **Preparation of Materials.**—The preparation, aqueous solution chemistry, and ultraviolet spectrum of the $[Au(dien)Cl]Cl_2$ used in this study were reported earlier.[3]

(B) **Kinetic Studies.**—Solutions of $[Au(dien)Cl]Cl_2$ were prepared by dissolving a weighed amount of the complex in distilled water and adding a few milliliters of 0.3 *M* $HClO_4$ until the pH was *ca.* 2.0–2.5. The addition of acid ensured that none of the conjugate base was present in the solution. Under these conditions, hydrolysis of the complex did not occur, as judged from the same ultraviolet spectrum with and without added chloride ion. Therefore, the kinetics investigated were for reaction 1.

$$[Au(dien)Cl]^{2+} + Y^- \longrightarrow [Au(dien)Y]^{2+} + Cl^- \quad (1)$$

Reactions of the conjugate base with various reagents were carried out by mixing an aqueous solution of $[Au(dien)Cl]^{2+}$ with a phosphate buffer of pH 7, which contained the desired reagent. Thus, at this pH, the Au(III) complex was converted instantaneously to the conjugate base (2). The reaction studied

$$[Au(dien)Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Au(dien\text{-}H)Cl]^+ + H_2O \quad (2)$$

then was that of the conjugate base with the added reagent (3).

$$[Au(dien\text{-}H)Cl]^+ + Y^- \longrightarrow [Au(dien\text{-}H)Y]^+ + Cl^- \quad (3)$$

Several kinetic runs were also carried out by allowing bromide ion to react with a solution of $[Au(dien\text{-}H)Cl]^+$ prepared from $[Au(dien)Cl]^{2+}$ and 1 equiv. of NaOH solution. The results were the same, within experimental error, as those obtained by allowing an aqueous solution of $[Au(dien)Cl]^{2+}$ to react with a phosphate buffer solution of pH 7 containing bromide ion. Thus, the buffer components do not affect the rate.

Kinetics of reaction 4 were studied by dissolving a weighed

$$[Au(dien)OH]^{2+} + Y^- + H^+ \longrightarrow [Au(dien)Y]^{2+} + H_2O \quad (4)$$

amount of $[Au(dien)X]^{2+}$ ($X^- = Cl^-, Br^-$) in water and adding 2 equiv. of NaOH solution, thereby producing $[Au(dien\text{-}H)OH]^+$ in solution. This solution was then mixed in the stopped-flow apparatus with a solution of NaY which contained sufficient $HClO_4$ to cause the pH of the reaction mixture to be in the desired range, usually between 1 and 2. The pH of the reaction mixture was obtained by measurement with a Beckman Model G pH meter.

Rates of all the reactions were determined spectrophotometrically by means of a stopped-flow apparatus, which consisted of a Beckman DU spectrophotometer to which was attached a rapid mixing device. These reactions were usually complete in 1 sec. or less. The change in percentage transmission with time at a convenient wave length as the reaction progressed was displayed on an oscilloscope. The oscilloscope trace was recorded permanently with a Polaroid camera. The reactions were made to go to completion by using an excess of reagent, usually more than ten times the complex concentration. The completeness of the reaction, as well as the nature of the product, was checked by recording the ultraviolet spectrum between 400 and 260 mμ on a Cary Model 11 or Beckman DK-2 spectrophotometer. Thus, the product of the reaction between $[Au(dien)Cl]Cl_2$ and bromide was identified by comparing a spectrum of the mixture with that of the known complex [Au-

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[1] For a review see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[2] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954). It has just come to our attention that a detailed kinetic study on the reaction of $AuCl_4^-$ with ethylenediamine has been reported (P. Beran and A. A. Vlček, *Collection Czechoslov. Chem. Commun.*, **24**, 3572 (1959).

[3] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poë, *Inorg. Chem.*, **2**, 921 (1963).

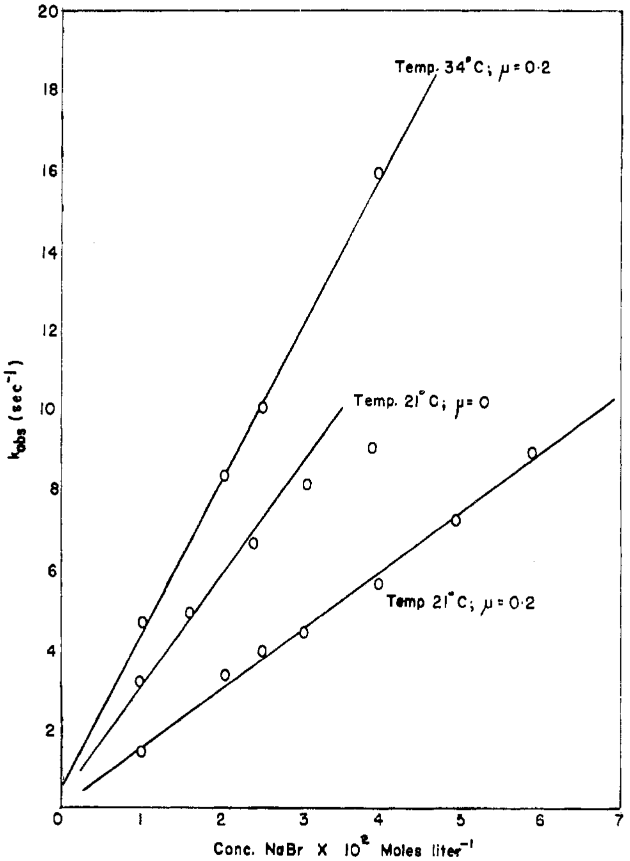

Fig. 1.—Dependence of k_{obsd} on bromide ion concentration for the reaction of $[Au(dien)Cl]^{2+}$ with this reagent.

(dien)Br]$^{2+}$. The final spectrum of the reaction between [Au-(dien-H)Cl]$^{+}$ and OH^- was the same as the spectrum of either $[Au(dien)Cl]^{2+}$ or $[Au(dien)Br]^{2+}$ to which 2 equiv. of OH^- had been added. The products of the reactions between [Au(dien-H)Cl]$^{+}$ and I^-, SCN^-, and N_3^- were not identified. However, for these reactions there was no spectral evidence of complications such as cleavage of the amine from the complex or reduction.

Pseudo-first-order rate constants were obtained graphically by means of the usual first-order plot. A plot of the experimentally observed rate constant against the reagent concentration yielded a straight line, with an intercept not significantly different from zero for most of the reagents studied. Some kinetic runs were made several times under the same conditions. Reproducibility was better than 5–10%.

Results

(A) Reactions of $[Au(dien)Cl]^{2+}$.—Unfortunately, kinetic studies of substitution reactions of this substrate were limited to just one reagent, bromide ion. Reagents such as iodide ion, thiocyanate ion, and thiourea reduced the complex, probably to a gold(I) species. Basic anions such as nitrite and azide could not be used because it was necessary to carry out the reactions in the pH range 2.0–2.5, since the complex functions as an acid with a pK_a of 4. Rate data for the reactions of $[Au(dien)Cl]^{2+}$ with bromide ion are listed in Table I. The effects of variations of bromide ion concentration, ionic strength, and temperature were investigated, and the results are shown graphically in Fig. 1. Since previous workers[4] observed that traces of Fe(II) in laboratory distilled water catalyzed the exchange of radiochloride with $AuCl_4^-$, the effect of Fe(II) on reaction 1 was tested. No significant change in rate was observed.

Table I

Rate Constants for the Reaction

$$[Au(dien)Cl]^{2+} + Br^- \xrightarrow{H_2O} [Au(dien)Br]^{2+} + Cl^-$$

pH 2.3 ($HClO_4$)

[NaBr], M	k_{obsd}, sec.$^{-1}$
21°; no inert salt added	
0.0098	3.2
0.0161	4.9
0.024	6.6
0.0308	8.1
0.0392	9.0
0.585	11
21°; μ = 0.2 with $LiClO_4$	
0.0101	1.4
0.0204	3.3
0.0251	3.9
0.0304	4.4
0.0397	5.6
0.0493	7 2
0.059	8.8
25°; no inert salt added	
0.0075	3.6
0.0127	5.2
0.0151	6.9
0.0199	8.5
0.00925	4.8[a]
0.0185	8.6[a]
34°; μ = 0.2 with $LiClO_4$	
0.0101	4.6
0.0204	8.3
0.0251	10
0.0397	16
0.059	24

[a] 10^{-6} M $FeSO_4$.

Figure 1 shows that there is a first-order dependence on bromide ion and that an increase in ionic strength decreases the rate very noticeably. The estimated rate constants and activation parameters are listed in Table II.

Table II

Rate Constants and Activation Parameters for the Reaction

$$[Au(dien)Cl]^{2+} + Br^- \xrightarrow{H_2O} [Au(dien)Br]^{2+} + Cl^-$$

Temp., °C.	Ionic strength	k_2, M^{-1} sec.$^{-1}$[c]
21	0.2[a]	154
21	[b]	270
25	[b]	380[d]
34	0.2[a]	387
ΔH^*		13 kcal.[e]
ΔS^*		−4 e.u.

[a] Ionic strength adjusted with $LiClO_4$. [b] No inert salt added, thus ionic strength was less than 0.05. [c] Values of k_1 were too small to be determined accurately in these experiments, but the limits are approximately $0.5 > k_1 > 0.0$. [d] Calculated from the initial linear portion of the k_{obsd} vs. $[Br^-]$ plot. [e] Calculated from the k_2 values at 21 and 34° where μ = 0.2 with $LiClO_4$.

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[4] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(B) Reactions of [Au(dien-H)Cl]$^+$.—This substrate reacted with several common reagents such as Br^-, I^-, SCN^-, N_3^-, and OH^- to give good kinetic results. Thiourea reduced the complex. Nitrite ion caused the spectrum of [Au(dien-H)Cl]$^+$ to change only a small amount.

Rate data are listed in Table III. The estimated values of k_2 are listed in Table IV, whereas the data from which they were obtained are plotted in Fig. 2. The slopes of the lines of Fig. 2 show that reactivity toward [Au(dien-H)Cl]$^+$ decreases in the order

$$I^- > SCN^- > Br^- > N_3^- > OH^- \sim H_2O \qquad (5)$$

which is generally the same as that observed for some similar Pt(II) complexes.[5] In the pH range 7.8–9.5 the reaction of the substrate with hydroxide is independent of pH. However, in more basic media, the rate increases and is dependent on the hydroxide concentration. Since complicating features such as olation and higher amido formation may occur in very basic solution, a quantitative kinetic study was not attempted at pH greater than 10.

TABLE III

RATE CONSTANTS AT 25° (pH 7)[a] FOR THE REACTION

$$[Au(dien\text{-}H)Cl]^+ + Y^- \xrightarrow{H_2O} [Au(dien\text{-}H)Y]^+ + Cl^-$$

[Y], *M*	k_{obsd}, sec.$^{-1}$
0.0099 Br^-	2.4
0.0202 Br^-	5.1
0.0347 Br^-	7.3
0.0456 Br^-	9.4
0.0026 I^-	17
0.0035 I^-	23
0.0052 I^-	33
0.0027 SCN^-	2.6
0.0047 SCN^-	4.8
0.0054 SCN^-	5.9
0.0071 SCN^-	7.7
0.0094 SCN^-	11
0.0050 N_3^-	1.0
0.0202 N_3^-	2.3
0 0405 N_3^-	3.9
0.081 N_3^-	5.8
pH 7.82 (OH^-)[b]	0.61
pH 8.52 (OH^-)[b]	0.62
pH 9.15 (OH^-)[b]	0.78
pH 9.52 (OH^-)[b]	0.65

[a] The reagent solution of pH of *ca.* 7 was prepared by dissolving NaY in 100 ml. of a buffer solution prepared from 50 ml. of 0.1 *M* KH_2PO_4 plus the requisite amount of 0.1 *M* NaOH and distilled water. [b] The buffer solutions in the pH range 7.8–9.5 were prepared by mixing 50 ml. of 0.1 *M* H_3BO_3 with the requisite amount of 0.1 *M* NaOH and diluting with water to 100 ml.

TABLE IV

FIRST-ORDER AND SECOND-ORDER RATE CONSTANTS FOR REACTIONS OF [Au(dien-H)Cl]$^+$ with Several REAGENTS IN WATER AT 25°

Reagent	k_1, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
I^-	[a]	6100
SCN^-	[a]	1300
Br^-	[a]	190
N_3^-	[a]	80
OH^-	0.6	0

[a] The extrapolated intercepts (k_1) are very small and cannot be determined accurately for these reagents where $k_2[Y^-]$ is much larger than k_1. However, its approximate limits are $1.0 > k_1 > 0.0$.

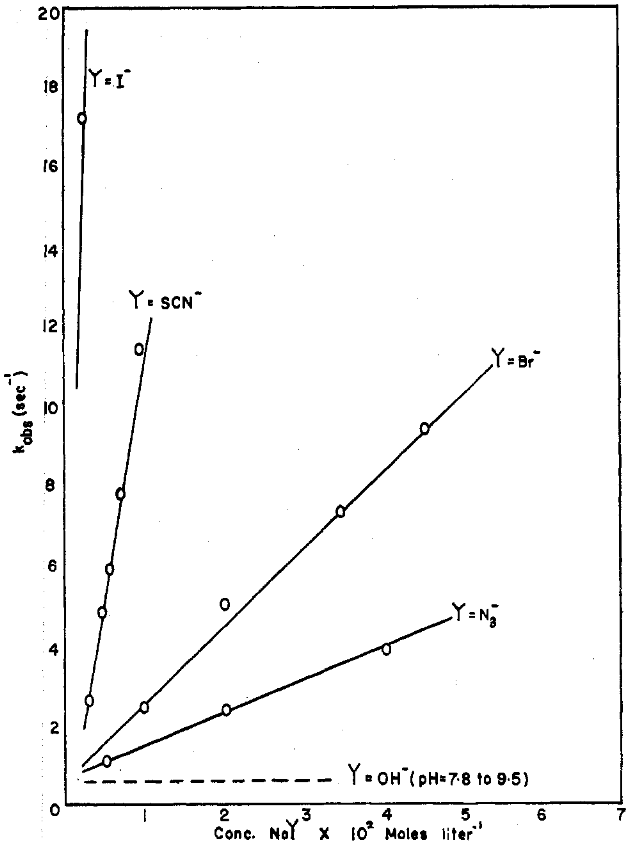

Fig. 2.—Dependence of k_{obsd} on the concentration of reagent (NaY) at 25° for the reaction of [Au(dien-H)Cl]$^+$ with NaY.

(C) Reactions of [Au(dien)OH]$^{2+}$.—Some rate data for a limited study of reaction 4 are given in Table V. For $Y^- = Cl^-$, the rate is first order in chloride

TABLE V

RATE DATA FOR THE REACTION AT 25° (5.6 × 10^{-4} *M* COMPLEX, IN WATER

$$[Au(dien)OH]^{2+} + Y^- \ (Y^- = Cl^-, Br^-) + H^+ \longrightarrow [Au(dien)Y]^{2+} + H_2O$$

[Y], *M*	pH[a]	k_{obsd}, sec.$^{-1}$
0.0040 Cl^-	2.36	8.5
0.0065 Cl^-	2.36	15
0.0089 Cl^-	2.36	20
0.0115 Cl^-	2.36	21
0.0139 Cl^-	2.36	28
0.0066 Cl^-	2.5	12
0.0066 Cl^-	1.8	19
0.0066 Cl^-	1.1	24
0.0066 Cl^-	0.8	21
0.0048 Br^-	2.4	[b]

[a] pH adjusted with $HClO_4$. [b] Complete in 30 msec.

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(5) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

TABLE VI

COMPARISON OF SOME Pt(II) AND Au(III) KINETIC DATA

	Reaction	k_1, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$	ΔH_1^*, kcal.	ΔH_2^*, kcal.	ΔS_1^*, e.u.	ΔS_2^*, e.u.
20°	$AuCl_4^- + {}^*Cl^{-a}$	0.006	1.47	4.5	16.5	−50	−2
	$[Au(dien)Cl]^{2+} + Br^-$	<0.5	154.	...	13	...	−4
25°	$PtCl_4^{2-} + {}^*Cl^{-b}$	3.8×10^{-5}	0	21	...	−8	...
	$[Pt(dien)Cl]^{+c} + Br^-$	8.0×10^{-5}	5.3×10^{-3}	18^d	14^d	-16^d	-23^d

[a] Taken from ref. 2. [b] Taken from ref. 6. [c] Taken from ref. 5 [d] These activation parameters were obtained from values of k_1 and k_2 measured by us at 35 and 50° in conjunction with k_1 and k_2 values at 25° in ref. 5.

ion at constant [H^+]. At constant chloride ion concentration, the rate is less than first order in [H^+]. For example, an increase in [H^+] by a factor of ten doubles the rate. When $Y^- = Br^-$, the reaction is too fast to measure with the stopped-flow apparatus at our disposal.

Discussion

The results described above will be discussed primarily by comparing them with data for analogous Pt(II) systems. Relevant data, for purposes of comparison, are given in Table VI.

The isoelectronic and isostructural substrates, $[Au(dien)Cl]^{2+}$ and $[Pt(dien)Cl]^+$, are exceedingly different in rates of reaction. However, the two react similarly in some ways. For example, the order of reagent reactivity (5) toward the two substrates is the same.[5] Thus, for both Pt(II) and Au(III) substrates, it is the polarizability of the nucleophile and not its basicity that determines its effectiveness as a reagent. The two-term rate law (6) has been proposed as being general for substitution reactions of square-planar complexes[1] and was shown to apply for the

$$k_{obsd} = k_1 + k_2[Y] \qquad (6)$$

substrates $[Pt(dien)X]^+$. For the analogous Au(III) complexes, however, it appears that the reagent-independent path (k_1) is almost negligible. As shown in Fig. 1 and 2, the intercepts are quite small, and it is difficult to say if a finite intercept does exist, except for hydroxide ion reacting with $[Au(dien\text{-}H)Cl]^+$. This is in contrast to the analogous Pt(II) system, where the first-order path is quite important, and sometimes predominant. It is interesting to note that the anionic complex, $PtCl_4^{2-}$, exchanges chloride ion by a first-order process only,[6] whereas $AuCl_4^-$ exchanges chloride by both a first-order and a second-order process.[2] These results for both the cationic and anionic Au(III) and Pt(II) complexes may be summarized by saying that the reagent-dependent path is more important for Au(III) than for Pt(II). This is perhaps to be expected because of the larger oxidation state of the gold(III) which will tend to make bond making more important than bond breaking relative to the analogous platinum(II) substrates.

The k_2 value for the reaction of $[Au(dien)Cl]^{2+}$ with bromide is between four and five orders of magnitude greater than k_2 for the analogous Pt(II) reaction. It has been suggested[7] that the faster (*ca.* 200 times) rate of chloride exchange in $AuCl_4^-$–$^*Cl^-$ compared to $PtCl_4^{2-}$–$^*Cl^-$ is indicative of an SN2 or even an SN2(lim) mechanism, in which bond making is the main feature. If one considers only the k_2 values for the $[M(dien)Cl]]^+$–Br^- reactions, a similar conclusion may be reached. However, since the enthalpies of activation are about the same for the k_2 paths, it seems that both bond making and bond breaking are involved in the transition state, although it cannot be stated on the basis of these results which is predominant. If both bond making and bond breaking are involved in the kinetic act, it is reasonable that the ΔH_2^* values are about equal. In going from $[Pt(dien)Cl]^+$ to $[Au(dien)Cl]^{2+}$, the M–Cl bond strength increases making bond breaking more difficult, but concurrently the larger charged ion forms a bond with the entering nucleophile more readily. Hence, the two opposing factors may result in a similar ΔH_2^*. It may be mentioned that on the basis of the limited amount of data now available, it does appear that for the Au(III) systems bond making is more important than bond breaking. Thus, the cation $[Au(dien)Cl]^{2+}$ reacts approximately 100 times faster than does the anion $[AuCl_4]^-$ (Table VI). Likewise, the complex $[Au(dien)Cl]^{2+}$ reacts faster than its conjugate base $[Au(dien\text{-}H)Cl]^+$. This is in accord with charge neutralization being more important than charge separation in the transition state.

The entropy contribution is responsible for Au(III) reacting much faster than Pt(II) *via* the k_2 path, the values of ΔS_2^* being −4 and −23 e.u. for the Au(III) and Pt(II) reactions, respectively. Both of these values are abnormal if it is assumed that the major contribution to ΔS_2^* arises from an electrostrictive effect imposed on the solvent in going from the reactants to the activated complex. Thus, when oppositely charged ions come together to form an activated complex in which there is charge neutralization, solvation solvent molecules are released and an increase in entropy is to be expected.[8] In the exchange reaction of radiochloride ion with $[Pt(NH_3)_3Cl]^+$, for example, ΔS_2^* was found to be +19 e.u.[9] However, the reactions of several complexes of the type *trans*-$[Pt(P(C_2H_5)_3)_2X_2]$, where $X^- = Cl^-, Br^-$, or I^-, with X^- and with NO_2^- have recently been found

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(6) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 199.

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 2nd Ed., 1961, p. 144.

(9) F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

to proceed with ΔS^* values of -20 to -30 e.u.[10] Of course, solvent electrostriction is not the only thing that contributes to the entropy of activation. If stringent stereochemical requirements exist in the transition state, then its formation is accompanied by a decrease in entropy. This may be more than sufficient to compensate for the positive entropy effect due to solvation. The results at hand are not numerous but do fit such an explanation. For example, the entropy of activation for the exchange of radiochloride ion with $[Pt(NH_3)_3Cl]^+$ is positive and that for the reaction of bromide ion with $[Au(dien)Cl]^{2+}$ is less negative than for the same reaction of $[Pt(dien)Cl]^+$. This suggests that solvation effects are more important for the first two complexes than for the last. Such is the case because $[Pt(NH_3)_3Cl]^+$ is smaller and $[Au(dien)Cl]^{2+}$ has a larger charge relative to $[Pt(dien)Cl]^+$. It is also in accord with the negative ΔS^* values found for the nonionic *trans*-$[Pt(P(C_2H_5)_3)_2X_2]$ systems, where solvation effects are small.

The k_1 path, as mentioned previously, is less important in the reactions of these Au(III) complexes than is the k_2 path, but the converse is true for Pt(II). In order to try to explain this difference between Au(III) and Pt(II), it would be desirable to compare the activation parameters of the k_1 paths. Unfortunately, k_1 is so small relative to $k_2[Br^-]$ for the reaction of $[Au(dien)Cl]^{2+}$ with Br^- that values of ΔH_1^* and ΔS_1^* were not obtained. For the $[Pt(dien)Cl]^+$–Br^- reaction, the activation parameters are given in Table VI. These data are consistent with the mechanistic path *via* the solvent route proposed by Gray and Olcott for $[Pt(dien)X]^+$ type complexes.[11] These workers suggested that the principal intermediate in the first-order path of Pt(II) reactions is an aquo complex formed by an S_N2 reaction with the solvent water. For Au(III) such an aquo intermediate would be expected to be a strong acid and would not exist in aqueous solutions in significant quantities except under extremely acid conditions. Over the pH range in which our experiments were carried out, the principal hydrolyzed species was undoubtedly a hydroxo complex, $[Au(dien)OH]^{2+}$ at the lower pH range and $[Au(dien\text{-}H)OH]^+$ in the pH 7 region. The question then arises as to what is the first-order path intermediate in the reaction of Au(III) complexes. As noted in the Results section, $[Au(dien)OH]^{2+}$ was generated *in situ* and allowed to react with bromide ion under the same conditions of acidity and bromide ion concentration at which the $[Au(dien)Cl]^{2+}$–Br^- reaction was carried out. A reaction occurred in which $[Au(dien)Br]^{2+}$ was formed too fast to measure with our stopped-flow system. This indicates that $[Au(dien)OH]^{2+}$ (or a species that is formed therefrom under these experimental conditions) is labile enough to serve as the first-order path intermediate.

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[10] A. Turco and U. Belluco, private communication.

[11] H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

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The Kinetics of Some Related Electron-Transfer Reactions[1]

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The kinetics of the oxidation of a number of substituted tris(1,10-phenanthroline) complexes of iron(II) by cobalt(III) in perchloric acid have been investigated by the use of a flow technique. The results are compared with other oxidation–reduction reactions involving the iron(II)–phenanthroline complexes. The oxidation of $Fe(dipy)_3^{2+}$, $Fe(dipy)_2(CN)_2$, $Fe(dipy)(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, and the corresponding phenanthroline complexes by cerium(IV) in sulfuric acid has also been investigated. It was found that the oxidation of the mixed-ligand complexes proceeds more rapidly than the oxidation of the complexes containing identical ligands. Other oxidation–reduction reactions studied include the oxidation of $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ by Ce(IV) and $IrCl_6^{2-}$, as well as the $Mo(CN)_8^{3-}$–$W(CN)_8^{4-}$, $Mo(CN)_8^{3-}$–$Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$–$W(CN)_8^{4-}$ reactions. The results are discussed in the light of the Marcus theory of electron-transfer reactions.

The *a priori* calculation of the rates of electron-transfer reactions requires a knowledge of such properties of the reactants and products as interatomic distances, force constants, etc.[2] Unfortunately, many of these quantities are not known at the present time for most electron-transfer reactions of interest. However, Marcus has shown that these parameters tend to cancel when reactions involving a series of related systems are compared.[3] Thus, to a very good approximation, it is not necessary to know the values of

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960).

[3] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).