Contribution from the National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria, South Africa

Kinetics and Mechanisms of Reactions of Gold(III) Complexes III. Substitution Reaction of Tetrachlorogold(III) with Ethylenediamine

W. J. Louw and W. Robb

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The kinetics of the reaction $[AuCl_4]^- + en \rightarrow$ *(where en is ethylenediamine), have been studied in acid medium at different temperature and pH values and the following reaction scheme is suggestd:*

$$\begin{tikzcd}[AuCl_3(OH)]^- + enH^+ \arrow[r, "k_1"] & {[AuCl_3(en)] + H_2O} \arrow[d, "fast"] \\ & {[AuCl_2(en)]^+ + Cl^-}\end{tikzcd}$$

$$\begin{tikzcd}[AuCl_2(en)]^+ + enH^+ \arrow[r, "k_2"] & {[AuCl(en)(enH]^{3+} + Cl^-} \arrow[d, "fast"] \\ & {[Au(en)_2]^{3+} + H^+ + Cl^-}\end{tikzcd}$$

Also included are some tentative results suggesting

$$[AuCl_2(en)]^+ + H_2O \overset{k_3}{\rightleftharpoons} [AuCl(H_2O)(en)]^{2+} + Cl^- .$$

At 25°C values of $k_1 = 4.7 \times 10^2\ M^{-1}\ sec^{-1}$, $k_2 = 1.72 \times 10^1\ M^{-1}\ sec^{-1}$, $k_3 = (1.2 \pm .7) \times 10^{-4}\ sec^{-1}$ *were obtained. The activation parameters were found to be:* $\Delta H_1^* = 15.6$ *kcal mole*$^{-1}$, $\Delta H_2^* = 13.8$ *kcal mole*$^{-1}$, $\Delta S_1^* = +6.0$ *e.u.*, $\Delta S_2^* = -7.0$ *e.u.*

Introduction

It is evident from some of the more recent writings and discussions that the existing dearth of information of the reaction rates of gold(III) complexes[1-6] is rapidly being augmented by systematic and comprehensive studies. The gross features of the mechanism of reactions of these square-planar complexes have been closely identified with those of the now very well documented isoelectronic platinum(II) complexes.[7-9] The two term rate law

$$k_{obs} = k_1 + k_2[Y] ,$$

for reactions such as $AuXA_2L + Y \rightarrow AuYA_2L + X$ has often been established by experimentation since it was first formulated by Rich and Taube[10] in 1954.

Further to our work in this laboratory in which the system $[AuCl_4]^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [AuCl_3(H_2O)] + Cl^-$, and subsequent acid hydrolysis of the aquochloroaurate(III), was studied,[3] followed more recently by studies on the $[AuBr_4]^-$,[11] the reaction between $[AuCl_4]^-$ and the bidentate ethylenediamine was deemed interesting enough to examine at this juncture. Very few examples of the reaction of gold(III) or even other metals that form square-planar complexes with polydentate ligands are to be found in the literature.[12-15]

The study reported here is compared to the polarographic study reported by Beran and Vlček[15] for the reaction between ethylenediamine and tetrachlorogold(III) in aqueous acid medium.

Experimental Section

$HAuCl_4$ Solutions. The $[HAuCl_4]$ used was a Merck product. An approximately $10^{-3}\ M$ solution was made up in a $2\ M$ NaCl (A.R. grade) medium to ensure that the only gold chloride species present are the $AuCl_4^-$ and $[AuCl_3(H_2O)]$. The latter dissociates[3] to $[AuCl_3(OH)]^- + H^+$, depending upon the pH chosen. The pH was adjusted with acetic acid/sodium acetate buffer and the ionic strength adjusted with sodium perchlorate (laboratory reagent grade).

Buffer Solutions. Buffer solutions were made according to the tables given in " Quantitative Analysis "[16] from $0.4\ M$ acetic acid and $0.4\ M$ sodium acetate solutions.

Ethylenediamine Solutions. The ethylenediamine dihydrochloride salt used was a B.D.H. Laboratory reagent, the purity of which was improved by re-

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(1) L. Cattalini, A. Orio, and M. L. Tobe, *Inorg. Chem.*, *6*, 75 (1967).
(2) L. Cattalini, A. Doni, and A. Orio, *ibid.*, *6*, 280 (1967).
(3) W. Robb, *ibid.*, *6*, 382 (1967).
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(7) F. Basolo and R. G. Pearson, " Mechanisms of Inorganic Reactions ", 2nd ed., John Wiley and Sons, Inc., New York (1967).
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(9) F. Basolo, in " Mechanisms of Inorganic Reactions ", Advances in Chemistry Series, *Am. Chem. Soc.*, *49* (1965).
(10) R. L. Rich and H. Taube, *J. Phys. Chem.*, *58*, 1 (1954).
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(13) P. Uguagliati, U. Belluco, U. Croatto, and R. Pietropaolo, *J. Am. Chem. Soc.*, 89, 1336 (1967).
(14) P. Haake and P. Cronin, *Inorg. Chem.*, *2*, 879 (1963).
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(16) A. I. Vogel, " Quantitative Inorganic Analyses ", Longmans, Green and Co. Ltd., London (1954).

crystallization from a water-alcohol mixture. The solution was buffered, ionic strength adjusted and made up in a 2 *M* NaCl medium as above mentioned.

pH Measurements. pH Measurements were made with a Metrohm Model E 300 pH-meter.

Kinetic Experiments. The $[AuCl_4]^-$ and ethylenediamine solutions were thermostated in a water-bath where temperatures were controlled to ±0.1°C. A measured aliquot was transferred to a cell housed in a constant temperature cell holder fitted to a Cary 15 recording spectrophotometer. Working at a constant wavelength of 313 mμ, a measured amount of ethylenediamine solution was injected into the gold solution. The volume ratio of the two solutions was chosen as such to give the wanted [en]. Effective mixing is achieved in not greater than 0.1 seconds, provided the volume ratio does not exceed 5:1. An excess of ethylenediamine was used in order to achieve pseudo-first-order conditions. A trace of the change in optical density with time was displayed on the chart.

Preparation of $[Au(en)_2Cl_3]$ *Complex.* The $[Au(en)_2Cl_3]$ complex was prepared according to the method of Block and Bailar Jr.[17] The complex was made up in solution similar to that of the above mentioned $[AuCl_4]^-$ solutions.

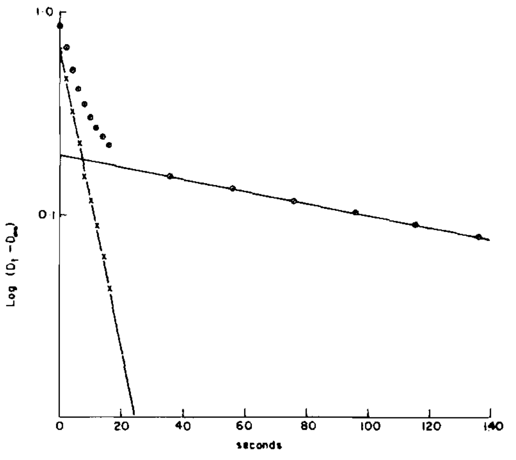

Figure 1. Log (D_t-D_∞) *vs.* time at 25°C, pH=5.35, $\mu=2.2$ for the reaction $[AuCl_2(en)]^+ + [enH]^+ \longrightarrow$

Results and Discussion

Figure 1 shows the plot of $\log(D_t-D_\infty)$ *vs.* time obtained from the reaction between $[AuCl_4]^-$ or $[AuCl_3(OH)]^-$ and ethylenediamine. Clearly two consecutive reactions are observed with a " fast " component going to completion some 30 times faster than a slow component. The " fast " and " slow " components may be resolved by a curve stripping technique into two straight lines from where the values for $k_{cbs}=\frac{.693}{t_{1/2}}$ were computed. After essentially following the first and faster reaction to completion, the chart speed was reduced by a factor of 10 as shown by Figure 2.

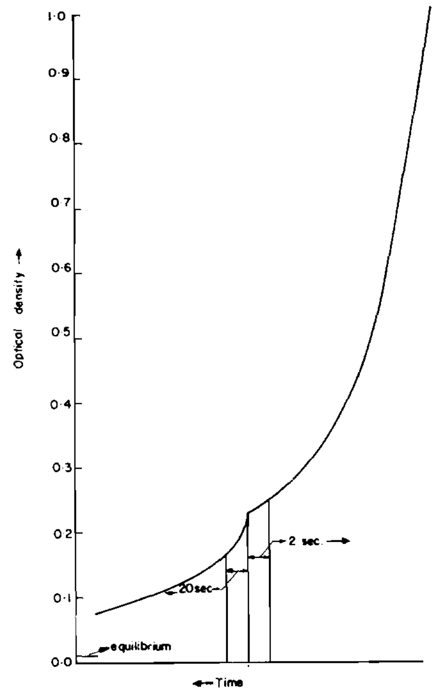

Figure 2. O.D. *vs.* time at 25°C, $\mu=2.2$, pH=5.35 for the reaction $[AuCl_2(en)]^+ + [enH]^+ \longrightarrow$

Plotting the k_{obs} values *vs.* $[enH_2^{2+}]$ yielded a straight line having a positive slope and no intercept for the fast component of the reaction. The slope of this line was shown to be inversely dependent upon the hydrogen ion concentration. The results of all of the experiments are sumarized in Table I. Column 4 of that table lists the $k_{obs(1)}$ values for the first substitution reaction. Treating the results of the second reaction likewise (Figure 3), it can be seen that the functional dependence of the $k_{obs(2)}$ on ethylenediamine concentration exhibits a very small but non-zero intercept. Once again the slope of the line exhibits an inverse hydrogen ion dependence whilst the intercept appears to remain quite insensitive to variations in the pH of the reactant solution within the limits of accuracy of the measurements.

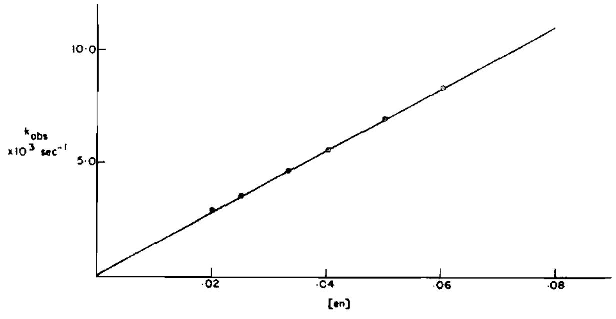

Figure 3. k_{obs} *vs.* [en] at 25°C, $\mu=2.2$, pH=5.35 for the reaction $[AuCl_2(en)]^+ + [enH^+] \longrightarrow$

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[17] B. P. Block and John C. Bailar, Jr., *J. Am. Chem. Soc., 73,* 4722 (1951).

Table I. Rate data for the substitution reactions.

$$[AuCl_3(OH)]^- + enH^+ \xrightarrow{k_1} [AuCl_3en] + H_2O \qquad (1)$$

$$k_{obs(1)} = \frac{k_1K_a[enH_2^{2+}]}{[H^+]}$$

$$[AuCl_2en]^+ + enH^+ \xrightarrow{k_2} [AuCl(en)(enH)]^{3+} + Cl^- \qquad (2)$$

$$[AuCl_2en]^+ + H_2O \overset{k_3}{\rightleftharpoons} [AuCl(en)(H_2O)]^{2+} + Cl^-$$

$$k_{obs(2)} = k_3 + \frac{k_2K_a[enH_2^{2+}]}{[H^+]}$$

[en]	pH	°C	$10^2k_{obs(1)}sec^{-1}$ [a]	$10^3k_{obs(2)}sec^{-1}$ [a]
0.060	5.35	25	23.00	8.34
0.050	5.35	25	17.80	6.86
0.040	5.35	25	14.80	5.52
0.033	5.35	25	11.50	4.60
0.025	5.35	25	8.70	3.65
0.020	5.35	25	7.00	2.90
0.120	4.8	25	—	4.90
0.100	4.8	25	10.70	4.05
0.080	4.8	25	8.30	3.35
0.066	4.8	25	6.85	2.8
0.050	4.8	25	4.85	2.1
0.040	4.8	25	3.85	1.7
0.066	4.3	25	2.12	.71
0.060	4.3	25	1.74	.64
0.050	4.3	25	1.53	.57
0.040	4.3	25	1.20	.47
0.033	4.3	25	1.01	.39
0.025	4.3	25	0.76	.34
0.020	4.3	25	0.61	.27
0.075	4.3	20	1.51	—
0.066	4.3	20	1.31	--
0.060	4.3	20	1.15	.403
0.050	4.3	20	0.99	.356
0.040	4.3	20	0.83	.290
0.033	4.3	20	0.68	.255
0.025	4.3	20	0.51	.205
0.020	4.3	20	0.44	.177
0.364 [b]	4.2	25	—	3.40
0.333	4.2	25	8.10	3.08
0.300	4.2	25	7.21	2.76
0.250	4.2	25	5.95	2.32
0.200	4.2	25	4.85	1.91
0.166	4.2	25	4.28	1.61
0.125	4.2	25	3.12	1.26
0.100	4.2	25	2.53	.99
0.333	4.2	30	—	5.15
0.300	4.2	30	11.55	4.70
0.250	4.2	30	9.75	3.92
0.200	4.2	30	7.65	3.33
0.167	4.2	30	6.25	2.75
0.125	4.2	30	4.60	2.26
0.100	4.2	30	3.95	1.78
0.300	4.2	35	18.2	7.70
0.250	4.2	35	15.0	6.50
0.200	4.2	35	12.4	5.50
0.166	4.2	35	10.0	4.80
0.125	4.2	35	8.0	3.75
0.100	4.2	35	6.0	3.10

[a] k_{obs} Values average of up to 5 values. [b] Above this point values were taken at $\mu = 2.3$, 2.2 Below this point values were taken at $\mu = 2.7$.

Before presenting any mechanistic arguments, it would be best to consider firstly some equilibria that are known to exist in solutions such as those under consideration. Firstly, the distribution of enH_2^{2+}, enH^+, and en at different pH values are given in Figure 4.[18] It is evident that the prime species present under the pH conditions selected for this experiment are enH_2^{2+} and enH^+ which are to be expected in an equilibrium represented by the equation

$$enH_2^{2+} \overset{K_a}{\rightleftharpoons} enH^+ + H^+$$

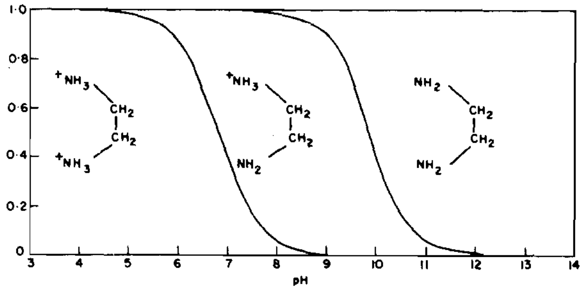

Figure 4. Distribution diagram for ethylenediamine at different pH value.[18]

in which the ratio $[enH_2^{2+}]/[enH^+] \gg 1$ according to the $pK_a = 7.49$.[19] Secondly, in a previous study[3] it was established that the equilibrium

$$\begin{tikzcd}[AuCl_4]^- + H_2O \arrow[r, leftrightharpoons] & {[AuCl_3(H_2O)] + Cl^-} \arrow[d, shift left, "K_a"'] \\ & {[AuCl_3(OH)]^- + H^+} \arrow[u, shift left]\end{tikzcd}$$

would favour the $[AuCl_4]^-$ species such that the ratio

$$[AuCl_4]^- / [AuCl_3(OH)^-] = 87 \text{ at pH} = 25°, [Cl^-] = 2\,M.$$

Two or more reaction possibilities present themselves for consideration in any attempt to account for the " fast " reaction described above. The most likely of these would be the reaction

$$[AuCl_3(OH)]^- + enH^+ \xrightarrow{k_1} [AuCl_3en] + H_2O.$$

followed by the rapid closing of the chelate ring with the expulsion of a *cis* chloride group, *viz.*

$$[AuCl_3en] \xrightarrow{fast} [AuCl_2en]^+ + Cl^-.$$

Alternatively, enH_2^{2+} may react with $[AuCl_3(OH)]^-$ or, for that matter enH^+ with $AuCl_4^-$ because the equilibrium between $[AuCl_4]^-$ and $[AuCl_3(OH)]^-$ can shift considerably faster than is the observed reaction with the ethylenediamine species. A clue as to the identity of the reacting ethylenediamine species is to be found in the inverse hydrogen ion concentration dependence of the first reaction. The observed rate constant may be formulated as follows:

$$k_{obs(1)} = k_1[enH^+] = k_1K_a\frac{[enH_2^{2+}]}{[H^+]}$$

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(18) J. N. Butler, " Ionic Equilibrium ", Addison-Wesley Publishing Company, Inc., Massachusetts, p. 233 (1964).

(19) The Chemical Society, Special Publication No. 6, " Stability Constants. Part I: Organic Ligands ", Metcalfe and Copper Ltd., London, p. 5 (1957) (K_a value at 25°C and 1 M KNO_3).

Table II. Variation of rate constants with [H^+], temp., and μ and activation parameters

Temp. °C	10^5[H^+] M	μ	Slope$_{(1)}$ M^{-1}sec^{-1}	10^5k$_1$k$_a$ sec^{-1}	Slope$_{(2)}$ M^{-1}sec^{-1}	10^7k$_2$k$_a$ sec^{-1}	10^4k$_3$ sec^{-1}
25	0.445	2.2	3.65±0.16	1.63±.07	.1355±.0015	6.00±.07	1.1
25	1.58	2.3	1.03±0.05	1.62±.09	.0397±.0008	6.30±.12	1.2
25	5.00	2.2	0.31±0.01	1.53±.05	.0094±.0002	4.70±.12	.9
20	5.00	2.2	0.20±0.01	1.01±.04	.0058±.0002	2.89±.11	.6
25	6.30	2.7	0.245±0.01	1.54±.06	.0089±.0001	5.60±.09	1.3
30	6.30	2.7	0.38±0.01	2.42±.04	.0140±.0001	9.00±.06	4.1
35	6.30	2.7	0.61±0.01	3.84±.09	.0226±.0005	14.30±.32	9.2
			E$_a$kcal/mole	16.2 ±.8		14.4 ±1.0	33.6
			ΔH*kcal/mole	15.6		13.8	33.0
			ΔF*kcal/mole	13.8		15.8	17.3
			ΔS*e.u.	+6.0		—7.0	+53

$K_a = 3.24 \times 10^{-8}$ or $pK_a = 7.49$[19] $\quad \text{Slope}_{(1)} = \dfrac{k_1K_a}{[H^+]} \quad \text{Slope}_{(2)} = \dfrac{k_2K_a}{[H^+]}$

hence an easy alternative to choose enH$^+$ as the reacting species. The equation may still be seen as conforming to the general two term rate expression for substitution at a square-planar complex site except that the solvent path has disappeared, a fact that points to the reaction between the [$AuCl_3(OH)$]$^-$ species rather than [$AuCl_4$]$^-$ itself.

The second and slower reaction is ascribed to the reaction between $AuCl_2en^+$ and enH$^+$ in a manner analogous to the entry of the first enH$^+$ into the square-planar complex. It cannot be ascribed to the ring closure act for several reasons. The studies reported by Wilkins *et al.*[12] have shown that the rate determining step in the reaction of metal complexes with multidentate ligands is usually the coordination of one end of the ligand, followed by ring closure. Secondly, our slower reaction is also ethylenediamine dependent, to an extent, a fact irreconciliable with a partly coordinated bidentate. Finally, the product of these reactions is found to be [$Auen_2$]$^{3+}$. The final spectrum of the reactant solution is identical to that of a freshly prepared solution of [$Auen_2$]$^{3+}$.

The results given in Figure 3 and column 5 of Table I can best the accommodated by the reaction sequence

$$\begin{tikzcd}[AuenCl_2]^+ + enH^+ \arrow[r] & [AuCl(en)(enH)]^{3+} + Cl^- \arrow[d, "fast"] \\ & [Auen_2]^{3+} + Cl^- + H^+\end{tikzcd}$$

thus accounting for the k$_2$ path in the reaction where

$$k_{obs(2)} = k_3 + k_2[enH^+] = k_3 + k_2K_a \frac{[enH_2^{2+}]}{[H^+]}$$

That the reaction was not merely an equilibration between [$Auen_2$]$^{3+}$ and [$AuenCl_2$]$^+$ can be amply demonstrated by the behaviour of [$Auen_2$]$^{3+}$ in 2 M Cl^- medium. The presence of the Cl^- does not change the spectrum to any measurable extent and similarly, the addition of chloride to the finally obtained solution from the reaction of [$AuCl_4$]$^-$ with ethylenediamine does not cause any change. The small intercept shown in Figure 3 for the slower reaction can perhaps be ascribed to the hydrolysis of [$AuenCl_2$]$^+$ according to the reaction

$$AuenCl_2^+ + H_2O \overset{k_3}{\rightleftharpoons} AuenCl(H_2O)^{2+} + Cl^-$$

This is a very slow reaction accompanied by the expected high energy of activation. It is not at all surprising to find here a solvent path manifesting itself in accord with all of the expectation of a square-planar substitution reaction in aqueous acid medium. The k$_3$ path appears to be both ethylenediamine and hydrogen ion concentration independent, both facts pointing to the participation of a solvent water molecule.

In conclusion, it is now possible to draw some comparison between this study and the polarographic study of [$AuCl_4$]$^-$ reacting with ethylenediamine as reported by Beran and Vlček.[15] Firstly, they did not take cognisance of the extent to which [$AuCl_4$]$^-$ hydrolyses in acid medium buffered at pH 4.8. Also, working as they did in .1-.5 M ethylenediamine medium, the rapid reaction reported in this study must have escaped the attention, since the $t_{1/2}$ at pH = 4.8, T = 20°C must be 5.6 and 2.1 seconds in .1 and .5 M [en], respectively. Hence, the substitution reaction, thought to be the entry of the first ethylenediamine group, was, in fact, the entry of the second ethylenediamine described in this paper by the rate constant k$_2$. It is significant that the energy of activation for the ethylenediamine dependent process was measured to be 16.5 kcal/mole, a value that differs not too much from our value of 14.4±1 kcal/mole for the k$_2$ path, and 16.2 kcal/mole for the k$_1$ path. However, the real differences or similarities lie in the values for k and PZ, since k$_1$ reported here is 60 times greater than their value (5 sec^{-1} M^{-1}) whilst k$_2$ reported here (8.9 sec^{-1} M^{-1}) is very nearly the same but the log PZ for k$_1$ is 14.44 compared to 11.64 for k$_2$ and their 12.91 value at 20°C. A rather puzzling feature of their report resides in the behaviour of the intercept towards variation in pH. The energy of activation for that reaction, as well as the rate, would suggest that it is merely the hydrolysis of the $AuCl_4^-$ species under those conditions of Cl^- and H^+ concentration, a comparison that has already been made in a previous paper.[3]