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Kinetics and Mechanism of the Reduction of Tetrachloroaurate(III) by Oxalate in Acidic Aqueous Solution

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The reduction of $AuCl_4^-$ by oxalate was studied for the acidity range $0.0 \leqq pH \leqq 3.5$, chloride concentration range $10^{-3} \leqq [Cl^-] \leqq 0.8 M$ and total oxalate concentration $\leqq 0.1 M$ at 25° C and 1.0 M ionic strength (perchlorate medium). Kinetic evidence for the participation of the species $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ is provided. The kinetic indication that the Au(III) equilibria are influenced by the presence of oxalic acid is confirmed by spectrophotometric measurements. The rate of reduction of $AuCl_4^-$ by oxalic acid is neglectable when compared with that for the reduction by bioxalate and oxalate ions. The suggested mechanism consists of substitution followed by redox reactions for which the reaction products are Au(I), Au(0) and CO_2.

Introduction

The kinetics of the hydrolysis reaction of $AuCl_4^-$ during which species such as $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ are formed, has been the topic of a number of papers[1–6]. The proposed equilibrations led to a better understanding of the substitution mechanism of $AuCl_4^-$ by ethylenediamine[7,8], diethylenetriamine[9] and a series of methyl substituted ethylenediamines[10]. The reactions between $AuCl_4^-$ and substituents thiomorpholine-3-one[11] and thiourea[12] are followed by redox reactions in which Au(I) species are produced. Kazakov *et al.*[13] studied the thermal decomposition of the $AuCl_4^-$ –oxalate system and reported a mechanism consisting of a substitution reaction followed by a redox reaction. Only limited kinetic data was reported in this investigation. The photochemical decomposition of the $AuCl_4^-$–oxalate system at $pH \leqq 1$ was recently investigated in our laboratory[14].

The complexity of the above-mentioned systems necessitates the study of the redox reaction of $AuCl_4^-$ by oxalate over a wide enough pH and $[Cl^-]$ range to distinguish between the decomposition kinetics of the various participating Au(III) and oxalate species.

Experimental

The test solutions comprised $1.5 \times 10^{-4} M$ $AuCl_4^-$ in $[\text{total oxalate}] \leqq 0.1 M$ (added as oxalic acid) and $10^{-3} \leqq [Cl^-] \leqq 0.8 M$ (added as NaCl) at $0.0 \leqq pH \leqq 3.5$. The acidities were obtained by additions of $HClO_4$ and NaOH and measured with a Pye Unicam 292 pH meter for $pH > 1.0$. The ionic strength of the test solutions was maintained at $1.0 M$ with $NaClO_4$. No buffer was added since oxalate solutions are self-buffering in the pH range concerned. Chemicals of analytical and reagent grade were used throughout the investigation.

The reactions were performed in the thermostated cell compartment of a Zeiss PMQ II spectrophotometer, the temperature being controlled within 0.1° C at 25° C. The changes in absorbance were recorded for different time intervals depending on the pH, [total oxalate] and $[Cl^-]$ of the reaction mixture. The spectra were recorded on a Unicam SP1800 spectrophotometer. The radiochemical analysis was effected by employing C^{14}-labelled oxalic acid and a liquid scintillation technique[15] to detect the radioactive carbon dioxide produced during the redox reaction.

Results and Discussion

Spectra of $AuCl_4^-$ were recorded for different $[Cl^-]$ at the various acidities chosen for this investigation. The spectra for pH 2.0 presented in Figure 1 are a typical example. The decrease in absorbance with decrease in $[Cl^-]$ is ascribed to the equilibria

$$AuCl_4^- + H_2O \underset{}{\overset{K_A}{\rightleftharpoons}} AuCl_3(OH_2) + Cl^- \qquad (A)$$

$$AuCl_3(OH_2) \overset{K_B}{\rightleftharpoons} AuCl_3(OH)^- + H^+ \qquad (B)$$

where $K_A = 0.95 \times 10^{-5} M$ and $K_B = 0.25 M$ at 25° C and ionic strength $2.0 M$ (ref. 6). The absorbances at 313 nm lead to a value of $[AuCl_4^-]$ that agrees with the value calculated from the above equilibria. The

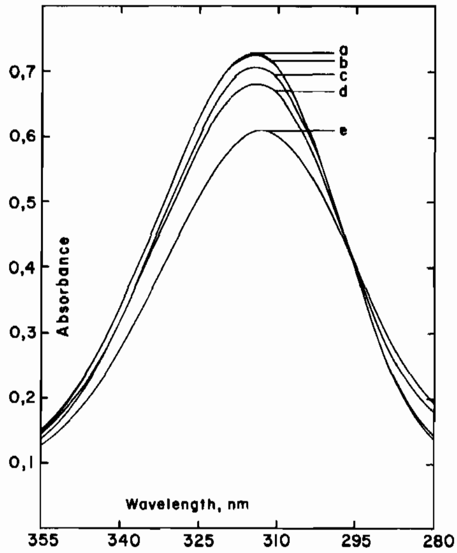

Figure 1. Spectra of $AuCl_4^-$ at pH 2.0. $[AuCl_4^-] = 1.5 \times 10^{-4} M$, Ionic strength = 1.0 *M*. a - $[Cl^-] = 1.0\ M$, b - $[Cl^-] = 0.1\ M$, c - $[Cl^-] = 0.01 M$, d - $[Cl^-] = 0.005 M$, e - $[Cl^-] = 0.001 M$.

spectrum for 1.0*M* Cl^- and pH 2.0 is exactly the same as that obtained for 1.0*M* HCl, in which it is known that all the Au(III) species are present as $AuCl_4^-$. The extinction coefficient for $AuCl_4^-$ is, therefore, $4.86 \times 10^3 M^{-1}\ cm^{-1}$ in good agreement with reported values[3,6]. An isosbestic point is observed at 296 nm in agreement with previous observations[3,5].

The observed first-order rate constants k_{obs} for the absorbance decrease at 313 nm on addition of oxalate was calculated from the conventional plot of $\log(A_t - A_\infty)$ *versus* t. These plots are linear for at least one half life. An excess of oxalate was maintained to ensure pseudo first-order conditions. Additional evidence for first-order behaviour is obtained from Table I, showing that k_{obs} is independent of $[AuCl_4^-]$. The rate constants for the various experimental conditions at 25° C were all determined for $[AuCl_4^-] = 1.5 \times 10^{-4} M$ and are summarized in Table II. The observed rate constant in absence of oxalate is neglectable when compared with the data in Table II. For 95% of the data, plots of k_{obs} *versus* [total oxalate] are linear and without intercept at constant pH and $[Cl^-]$ (*cf.* Figure 2). The data indicated by an asterisk (Table II) is not taken into consideration for the immediate discussion since k_{obs} *versus* [total oxalate] approaches a limiting value as illustrated in Figure 2.

TABLE I. Observed Pseudo First-Order Rate Constant k_{obs} as a Function of $[AuCl_4^-]$ at 25° C.

pH = 2.5	$[Cl^-] = 0.1\ M$, [total oxalate] = 0.055 *M*				
$[AuCl_4^-] \times 10^4$, *M*	1.5	1.25	1.0	0.75	0.5
$k_{obs} \times 10^4$, sec^{-1}	8.08	8.25	7.97	8.13	7.5

The remaining data conform to the equation

$$k_{obs} = k[\text{total oxalate}]$$

The values of the second-order rate constants k summarized in Table III, increase with a decrease in $[H^+]$ and $[Cl^-]$. At a given pH a plot of k *versus*

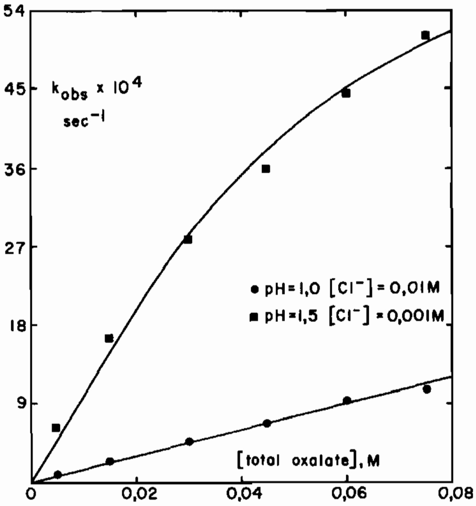

Figure 2. k_{obs} *versus* [total oxalate] for various pH and $[Cl^-]$ at 25° C.

TABLE II. Observed Pseudo First-Order Rate Constant k_{obs} as a Function of pH, $[Cl^-]$ and [total oxalate] at 25° C.

[total oxalate] *M*		0.10	0.085	0.075	0.070	0.060	0.055	0.045	0.040	0.035	0.030	0.025	0.015	0.005
pH	$[Cl^-]$	$k_{obs} \times 10^4$ (sec^{-1})												
0.0	0.1	0.41	0.36		0.30		0.23		0.16			0.10		
	0.01	1.34	1.13		0.93		0.84		0.61			0.41		
	0.005	2.88	2.52		2.07		1.56		1.13			0.75		
	0.002	5.50	4.71		3.82		3.40		2.46			1.52		
	0.001	10.50	8.88		7.22		5.66		4.71			3.21		

TABLE II. (Cont.)

[total oxalate] *M*		0.10	0.085	0.075	0.070	0.060	0.055	0.045	0.040	0.035	0.030	0.025	0.015	0.005
pH	$[Cl^-]$	$k_{obs} \times 10^4$ (sec^{-1})												
0.5	0.8	0.95	0.82		0.65		0.52		0.37			0.24		
	0.1	1.40	1.19		1.01		0.81		0.50			0.44		
	0.01	4.71	4.16		3.46		2.51		1.88			1.21		
	0.002	19.57	17.36		15.19		13.20		9.62			6.41		
	0.001	34.81	30.21		25.86		21.65		15.75			10.21		
1.0	0.8			1.69		1.34		0.98			0.61		0.34	0.12
	0.1			2.74		2.13		1.64			1.12		0.51	0.20
	0.01			10.40		9.02		6.95			4.65		2.55	0.87
	0.002			35.00		30.39		23.21			13.83		7.40	2.79
	0.001			51.79		42.00		33.97			23.24		12.19	5.21
1.5	0.8			3.66		3.20		2.24			1.67		0.92	0.58
	0.1			6.41		4.81		3.85			3.04		1.77	0.80
	0.01			14.43		11.78		9.54			7.21		3.98	1.80
	0.002			48.61		42.26		33.00			18.43		10.56	3.72
	0.001			50.95[a]		44.42[a]		36.09[a]			27.94		16.34	6.56
2.0	0.8			6.27		4.89		4.18			2.77		1.48	0.84
	0.1			6.79		6.48		4.73			3.75		2.02	0.62
	0.01			22.65		17.63		14.71			10.41		5.60	2.03
	0.002			49.85[a]		46.82[a]		46.20[a]			33.64		19.91	7.21
	0.001			64.16[a]		59.84[a]		46.76[a]			38.50		24.21	10.69
2.5	0.8						5.94	4.83		3.74		2.57	1.82	0.87
	0.1						7.35	5.89		4.81		4.01	2.21	1.19
	0.01						23.85	19.88		14.08		8.88	5.77	2.00
	0.002						64.76	66.63		56.80		38.50	16.98	9.62
	0.001						60.79[a]	58.23[a]		51.71		40.76	28.63	11.55
3.0	0.8						8.52	6.61		5.39		3.53	2.12	0.91
	0.1						9.16	7.91		6.01		5.37	4.03	1.66
	0.01						26.65	23.10		19.69		12.21	9.31	3.12
	0.005						53.31	45.29		32.21		20.87	14.68	6.06
	0.0025						66.63	56.34		38.50		34.65	21.12	8.70
	0.001						77.00[a]	69.30[a]		58.23[a]		51.33[a]	33.97	15.07
3.5	0.8						13.95	11.66		9.16		7.13	5.15	2.05
	0.1						16.17	13.43		11.00		8.55	6.27	2.55
	0.05						21.79	19.91		18.33		11.90	7.80	3.52
	0.025						32.08	24.40		19.91		16.82	11.62	4.39
	0.015						33.97	27.07		23.25		18.83	13.02	5.89
	0.010						46.82	37.25		31.78		26.25	18.43	8.21

[a] Values that are not included in the empirical rate law–see the discussion.

TABLE III. Second-Order Rate Constant k as a Function of pH and $[Cl^-]$.

pH	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
$[Cl^-]$, M	$k \times 10^3$, $M^{-1} sec^{-1}$							
0.8	–	0.95	2.20	5.33	8.89	10.9	14.9	27.1
0.1	0.42	1.42	3.61	8.89	11.1	14.0	18.7	32.0
0.05	–	–	–	–	–	–	–	45.7
0.025	–	–	–	–	–	–	–	60.0
0.015	–	–	–	–	–	–	–	68.0
0.01	1.40	4.78	14.7	21.0	31.4	41.6	52.3	93.3
0.005	2.90	–	–	–	–	–	95.9	–
0.0025	–	–	–	–	–	–	125	–
0.002	5.67	21.6	47.9	67.8	110	150	–	–
0.001	10.6	36.6	72.7	100	141	170	248	–

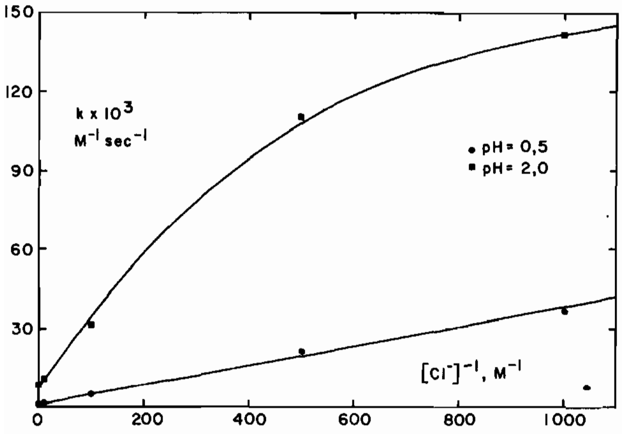

Figure 3. k *versus* $[Cl^-]^{-1}$ for various pH at 25° C.

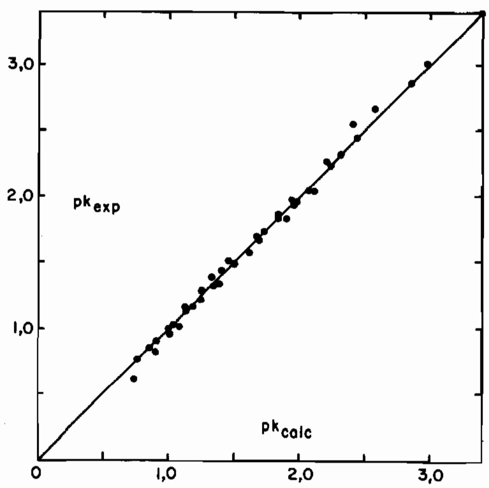

Figure 4. Relation between the experimental and calculated second-order rate constant k for all experimental conditions.

$[Cl^-]^{-1}$ is either linear with an intercept ($pH \leqq 0.5$) or initially linear and curved at higher $[Cl^-]^{-1}$ ($pH \geqq 1.0$) as illustrated in Figure 3. The $[Cl^-]$ dependence of k can be expressed as

$$k = \frac{k_a[Cl^-] + k_b}{[Cl^-] + k_c}$$

where k_a, k_b and k_c are $[H^+]$ dependent constants. For the data at $pH \leqq 0.5$ $[Cl^-] \gg k_c$ and the rate law simplifies to

$$k = k_a + \frac{k_b}{[Cl^-]}$$

where k_a is the intercept and k_b the slope of the plot of k *versus* $[Cl^-]^{-1}$. This limiting form of the rate law is also applicable to the initial linear part of the plots at $pH \geqq 1.0$. For these, k_c may be determined from a curve-fitting procedure provided that k_a and k_b are known. The values of k_a, k_b and k_c are summarized in Table IV. The validity of the empirical rate law was proven by recalculation of k using the data in Table IV. Figure 4 presents a logarithmic plot of the observed *versus* the calculated values of the second-order rate constant k (pk = –logk). We conclude that the empirical rate law provides a good description of the observed data.

TABLE IV. Values of the Empirical Constants k_a, k_b and k_c for Various pH.

pH	$k_a \times 10^3$ M^{-1} sec^{-1}	$k_b \times 10^4$ sec^{-1}	$k_c \times 10^4$ M
0.0	0.29	0.11	–[a]
0.5	1.0	0.38	–[a]
1.0	2.5	1.07	5.04
1.5	6.0	1.60	6.62
2.0	8.0	3.10	12.5
2.5	10.0	4.45	16.7
3.0	14.0	5.01	17.9
3.5	23.0	10.0	31.8

[a] k_c cannot be determined experimentally since $[Cl^-] \gg k_c$ and k *versus* $[Cl^-]^{-1}$ is without any curvature.

The suggested reaction mechanism combines equilibria (A) and (B) and reactions (1) to (6):

$$\left.\begin{aligned}
&AuCl_4^- + H_2C_2O_4 \xrightarrow{K_1'} AuCl_3(C_2O_4H)^- + HCl \\
&AuCl_4^- + HC_2O_4^- \xrightarrow{k_1''} AuCl_3(C_2O_4H)^- + Cl^- \\
&AuCl_4^- + C_2O_4^{2-} \xrightarrow{k_1'''} AuCl_3(C_2O_4)^{2-} + Cl^-
\end{aligned}\right\} (1)$$

$$\left.\begin{aligned}
&AuCl_3(OH_2) + H_2C_2O_4 \xrightarrow{K_2'} \\
&\qquad AuCl_3(C_2O_4H)^- + H_3O^+ \\
&AuCl_3(OH_2) + HC_2O_4^- \xrightarrow{K_2''} \\
&\qquad AuCl_3(C_2O_4H)^- + H_2O \\
&AuCl_3(OH_2) + C_2O_4^{2-} \xrightarrow{K_2'''} \\
&\qquad AuCl_3(C_2O_4)^{2-} + H_2O
\end{aligned}\right\} (2)$$

$$\left.\begin{aligned}
&AuCl_3(OH)^- + H_2C_2O_4 \xrightarrow{K_3'} \\
&\qquad AuCl_3(C_2O_4H)^- + H_2O \\
&AuCl_3(OH)^- + HC_2O_4^- \xrightarrow{k_3''} \\
&\qquad AuCl_3(C_2O_4H)^- + OH^- \\
&AuCl_3(OH)^- + C_2O_4^{2-} \xrightarrow{k_3'''} \\
&\qquad AuCl_3(C_2O_4)^{2-} + OH^-
\end{aligned}\right\} (3)$$

$$AuCl_3(C_2O_4H)^- \xrightarrow{k_4} AuCl_2(C_2O_4)^- + HCl \quad (4)$$

$$AuCl_3(C_2O_4)^{2-} \xrightarrow{k_5} AuCl_2(C_2O_4)^- + Cl^- \quad (5)$$

$$AuCl_2(C_2O_4)^- \xrightarrow{K_6} AuCl_2^- + 2CO_2(\uparrow) \quad (6)$$

The reactions (1)–(6) include a series of substitution reactions (1)–(3), followed by ring-closure (4) and (5) and a rapid two-electron transfer reaction (6). The rate-determining steps are reactions (1)–(3) and $k_6 \gg k_5$, $k_4 > k_1$, k_2, k_3. Three Au(III) chloride and three oxalate species participate in the process. The theoretical rate law for the suggested mechanism is

$$-\frac{d}{dt}[Au(III)] = \{k_1[AuCl_4^-] + k_2[AuCl_3(OH_2)] + k_3[AuCl_3(OH)^-]\}[\text{total oxalate}]$$

where k_1, k_2 and k_3 are overall $[H^+]$ dependent rate constants, *viz.*

$$k_1 = k_1' f_{H_2Ox} + k_1'' f_{HOx^-} + k_1''' f_{Ox^{2-}}$$
$$k_2 = k_2' f_{H_2Ox} + k_2'' f_{HOx^-} + k_2''' f_{Ox^{2-}}$$
$$k_3 = k_3' f_{H_2Ox} + k_3'' f_{HOx^-} + k_3''' f_{Ox^{2-}}$$

In these expressions

f_{H_2Ox} = fraction of total oxalate present as $H_2C_2O_4$ $= 1/K$

f_{HOx^-} = fraction of total oxalate present as $HC_2O_4^-$ $= K_1/[H^+]K$

$f_{Ox^{2-}}$ = fraction of total oxalate present as $C_2O_4^{2-}$ $= K_1K_2/[H^+]^2 K$

with

$$K = 1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}$$

and K_1, K_2 = dissociation constants for oxalic acid determined as 3.4×10^{-2} and $5.4 \times 10^{-4} M$ respectively at 25° C and ionic strength $1.0 M$ (perchlorate medium).

Inclusion of the equilibria (A) and (B) in the theoretical rate law leads to the expression

$$-\frac{d}{dt}[Au(III)] = \left\{\frac{k_1[H^+][Cl^-] + k_2K_A[H^+] + k_3K_AK_B}{[H^+][Cl^-] + K_A[H^+] + K_AK_B}\right\} \times [\text{total Au(III)}][\text{total oxalate}]$$

Thus k_{obs} = k[total oxalate]

$$\text{where } k = \frac{k_1[H^+][Cl^-] + k_2K_A[H^+] + k_3K_AK_B}{[H^+][Cl^-] + K_A[H^+] + K_AK_B} = \frac{k_1[Cl^-] + k_2K_A + \{k_3K_AK_B/[H^+]\}}{[Cl^-] + K_A + \{K_AK_B/[H^+]\}}$$

This expression is in agreement with the empirical rate law such that

$$k_a = k_1$$
$$k_b = k_2K_A + \{k_3K_AK_B/[H^+]\}$$
$$\text{and} \quad k_c = K_A + \{K_AK_B/[H^+]\}$$

The above relations render k_a, k_b and k_c $[H^+]$ dependent in agreement with Table IV. It follows from literature values of K_A and K_B (ref. 6) that $[Cl^-] \gg K_A + \{K_AK_B/[H^+]\}$ at $pH \leqq 0.5$, so that a plot of k *versus* $[Cl^-]^{-1}$ should be linear and with an intercept. This limiting form is also valid for the initial linear part of the plots of k *versus* $[Cl^-]^{-1}$ at $pH \geqq 1.0$. Previous investigations[7,8,9] led to similar linear plots, the absence of any curvature being possibly due to the limited range in which the $[Cl^-]$ was varied.

From a comparison of the empirical and theoretical rate laws it is possible to make certain deductions regarding the values of the equilibrium and rate constants. The values of k_a in Table IV are the values for k_1, the rate constant for the reaction of $AuCl_4^-$ with the various oxalate species. A plot of k_1 *versus* pH clearly shows two inflections at pH ~ 1.4 and ~ 3.5. These values are in good agreement with the earlier reported pK values for oxalic acid determined by pH titration. From the equation

$$k_1 = k_1' f_{H_2Ox} + k_1'' f_{HOx^-} + k_1''' f_{Ox^{2-}}$$

k_1', k_1'' and k_1''' can be calculated since k_1 is known for various pH[17]. The calculated values are $k_1' \sim 0$, $k_1'' = 10 \times 10^{-3}$ and $k_1''' = 27.6 \times 10^{-3} M^{-1} sec^{-1}$. The value of k_1' is neglectibly small as was previously reported[13]. A similar result was obtained for the reduction of $AuBr_4^-$ by oxalic acid[16]. The value for k_1'' at 25° C is in very good agreement with the previously reported value of $4.98 \times 10^{-3} M^{-1} sec^{-1}$ at 20° C and $25.8 \times 10^{-3} M^{-1} sec^{-1}$ at 40° C (ref. 13). The reaction involving oxalate (k_1''') is considerably faster than that involving bioxalate (k_1''), a feature also reported for the analogous reactions of $AuBr_4^-$ (ref. 16). The ratio k_1'''/k_1'' approximately equals 3, which compares favourably with similar ratios reported for substitution reactions in which oxalate is the entering ligand[17]. The equilibrium constants K_A and K_B can be calculated using the expression for k_c and the values in Table IV under certain conditions. According to literature $K_B = 0.25 M$ (ref. 6) such that $K_AK_B/[H^+] \gg K_A$ at pH ≧ 1.5, simplifying the expression for k_c to $k_c = K_AK_B/[H^+]$. The factor K_AK_B was calculated from the latter, the values being summarized in Table V (column 3). A principal feature of these values is their pH dependence, which is ascribed to the role played by the oxalate system. Apparently the presence of oxalic acid causes the Au(III) equilibria to shift in such way as to increase the value of K_AK_B (see further discussion). A similar effect was observed for the reduction of $AuCl_4^-$ by formic acid[18]. A possible explanation is the formation of an ion-pair between Cl^- and the carboxylic acid, causing a decrease in the rate of the chloride anation reaction of $AuCl_3(OH_2)$ and an increase in the value of K_A. The formation of such ion-pair was recently suggested for a similar system[10]. Having assumed that K_B should be independent of the presence of oxalic acid and that the effect on K_A should reach a limit at pH ≦ 1.0 (pK of oxalic acid equals

TABLE V. Equilibrium and Rate Constants Calculated from the Kinetic Data.

pH	$K_A + \{K_AK_B/[H^+]\}$, M[a]	$K_AK_B \times 10^5$, M^2	$k_2K_A + \{k_3K_AK_B/[H^+]\} \times 10^4$, sec^{-1}[b]	k_3 $M^{-1} sec^{-1}$	$k_2 = k_3$ $M^{-1} sec^{-1}$[c]	Equilibrium Data Determined Experimentally		
						$K_A + \{K_AK_B/[H^+]\} \times 10^4$ M[d]	Experimental Conditions $[Cl^-]$, M	[total oxalate], M
0.0	1.80[e]	3.60[f]	0.11	–	0.061	1.24	0.001	0.07
0.5	2.57[e]	3.60[f]	0.38	–	0.147	0.96	0.001	0.07
1.0	5.04	3.60[g]	1.07	–	0.212	2.98	0.001	0.075
1.5	6.62	2.09	1.60	0.242	–	3.44	0.001	0.075
2.0	12.5	1.25	3.10	0.248	–	3.90	0.001	0.07
2.5	16.7	0.53	4.45	0.266	–	7.59	0.001	0.07
3.0	17.9	0.18	5.01	0.280	–	15.0	0.001	0.07
3.5	31.8	0.10	10.0	0.314	–	47.4	0.01	0.07

[a] Experimental values of k_c in Table IV unless otherwise indicated. [b] Experimental values of k_b in Table IV. [c] Calculated from k_b/k_c when it is assumed that $k_2 = k_3$ (see discussion). [d] Equilibrium constants measured in the presence of oxalate (see discussion). [e] Calculated values of k_c when it is assumed that $K_A = 1.44 \times 10^{-4}$ M and $K_B = 0.25$ M (ref. 6) (see discussion). [f] It is assumed that K_AK_B is a constant at pH $\leqq$ 1.0 (see discussion). [g] Calculated from k_c when it is assumed that $K_B = 0.25$ M (ref. 6) (see discussion).

1.47 for the present system), we calculated the values of K_AK_B at pH $\leqq$ 1.0 (*cf.* Table V) to predict values for k_c at pH 0.0 and 0.5 since these could not be determined from the experimental data. Hence these assumptions enabled us to predict values for k_2 and k_3 at pH $\leqq$ 1.0 (see further discussion).

An attempt was made to measure the values of K_A and K_B in the presence of oxalate at various pH. The absorbance *versus* time traces were recorded for various reaction mixtures as shown in Table V (last column). The back extrapolation to the point of mixing yielded a value for the absorbance of $AuCl_4^-$ in the presence of oxalate at zero time. From the equation

$$[AuCl_4^-] = \frac{[H^+][Cl^-]}{[H^+][Cl^-] + K_A[H^+] + K_AK_B} \times [\text{total Au(III)}]$$

the value of $K_A + \{K_AK_B/[H^+]\}$ was calculated as a function of pH. These values (Table V, column 7) show exactly the same tendency as the kinetically determined values of k_c (Table V, column 2). The influence of oxalate is observed mainly at pH $\leqq$ 2.0 where oxalic acid is present in appreciable quantities. At pH > 2.5 a value of 0.15×10^{-5} was obtained for K_AK_B in good agreement with values (determined in the absence of oxalate) reported in literature[1,2,5,6]. Apparently the presence of bioxalate and oxalate ion has no influence on the equilibrium, in line with the idea of ion-pair formation between Cl^- and oxalic acid since such ion-pair formation will not occur between Cl^- and bioxalate/oxalate ion. We conclude that the pH dependence of K_AK_B is mainly due to an interaction with oxalic acid.

From the expression for k_b and its values in Table IV, the rate constants k_2 and k_3 can be calculated under certain conditions. Since k_2 and k_3 are of the same magnitude (see further discussion), it follows that $k_2K_A \ll k_3K_AK_B/[H^+]$ at pH$\geqq$1.5. The values of k_3 were calculated from k_b/k_c at pH$\geqq$1.5 and summarized in Table V (column 5). At pH $\leqq$ 1.0 this simplification is not valid and the assumption is made that k_2 and k_3 are approximately equal. The values for k_2 and k_3 in this pH range cannot be calculated unless this assumption is made. An identical situation was reported for the anation of $Co(NH_3)_5OH_2^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$ by oxalate[17,19], in which the participation of $Co(NH_3)_5OH^{2+}$ and $Cr(NH_3)_5OH^{2+}$ respectively was not kinetically identifiable. The value of k_3 (= k_2) at pH $\leqq$ 1.0 was once again calculated from k_b/k_c. A plot of k_3 as a function of pH is presented in Figure 5. Inflections are observed at pH ~0.5 and ~3.5, which corresponds satisfactorily with the pK values for $AuCl_3(OH_2)$ (pK_B) and $HC_2O_4^-$ (pK_2) respectively. We conclude

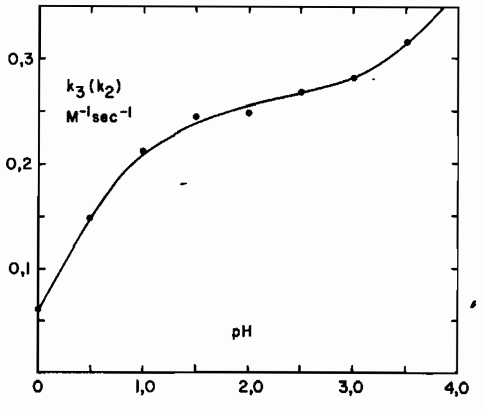

Figure 5. $k_3(k_2)$ as a function of pH.

that the rate constants for the reactions of $AuCl_3(OH_2)$ with $H_2C_2O_4$ (k_2'), $AuCl_3(OH)^-$ with $HC_2O_4^-$ (k_3'') and $AuCl_3(OH)^-$ with $C_2O_4^{2-}$ (k_3''') are approximately 0.05, 0.25 and 0.35 M^{-1} sec^{-1} respectively. These values suggest that the reactions involving the $AuCl_3$ species (k_2 and k_3) are much faster than those involving the $AuCl_4^-$ species (k_1). This is attributed to the easier displacement of an OH^-/OH_2 group than a chloride ion as reported for several analogous systems[8,9,10]. Despite the assumption made to calculate k_2 ($= k_3$) at pH $\leqq$ 1.0, the obtained value of k_3'' is in good agreement with that reported by Kazakov *et al.*[13] We also note that the reactivity of the $AuCl_3(OH)^-$ species is not as pH dependent as the $AuCl_4^-$ species.

The substitution reactions (1) to (3) are followed by the ring-closure reactions (4) and (5) that are normally non rate-determining. Under certain extreme conditions the rate of the substitution process, which depends on $[H^+]$, $[Cl^-]$ and [total oxalate], may exceed that of the ring-closure reactions such that the latter become rate-determining. This is probably the case with the data indicated by an asterisk in Table II. The ring-closure is independent of [total oxalate] and k_{obs} *versus* [total oxalate] will approach a limiting value. This value should vary with pH since the rate of ring-closure for $AuCl_3(C_2O_4H)^-$ and $AuCl_3(C_2O_4)^{2-}$ (*i.e.* k_4 and k_5) should differ to some extent. According to the values of k_{obs} in Table II, $k_4 \sim 5 \times 10^{-3}$ sec^{-1} and $k_5 \sim 7 \times 10^{-3}$ sec^{-1} at 25° C using an estimated pK value of ~2.0 (ref. 20) for $AuCl_3(C_2O_4H)^-$. Such rapid ring-closure reactions have been reported for analogous systems[7,10]. An alternative explanation for the occurrence of a limiting value of k_{obs} is the possibility that the aquation of $AuCl_4^-$ may become the rate-determining step under these conditions. In such case the reaction becomes less than first-order in oxalate. The rate of aquation of $AuCl_4^-$ is reported as 2.2×10^{-2} sec^{-1} in literature[4], which is approximately three times faster than the highest values of k_{obs} reported in Table II. Thus equilibrium is maintained throughout and our first explanation is favoured.

The ring-closing steps are followed by a rapid two-electron transfer reaction (6) which is non rate-determining. The species $AuCl_2^-$ is suggested to be the reaction product, although the presence of Au(0) is not excluded. Other species such as $Au(C_2O_4)^-$ and $Au(C_2O_4)_2^{3-}$ may also be present in an excess of oxalate[16].

Kazakov *et al.*[13] suggested a general mechanism of the type

$$AuCl_4^- + B \xrightarrow{k_7} AuCl_nB \xrightarrow{k_8} AuCl_2^- + OB$$

where B is the reducing agent and OB the oxidised form of B. They stated that $k_8 \gg k_7$ when B is oxalate. Applied to this study, the intermediate $AuCl_nB$ is suggested to be $AuCl_2(C_2O_4)^-$, which undergoes reduction prior to further substitution to produce species such as $Au(C_2O_4)_2^-$. A second substitution process usually produces a second "slower" reaction detectable from the pseudo first-order plots. This occurred for reactions with ethylenediamine[7] and thiourea[12] but was not observed for the present system.

TABLE VI. Radiochemical Results.

pH = 2.5; $[Cl^-] = 0.1$ *M*; [total oxalate] = 0.0005 *M*
Temp = 25° C $C^{14} = 1.0 \mu Ci/20$ ml test solution

Absorbance at 313 nm	0.67	0.58	0.48	0.41	0.32
Count Rate[a]	8590	20900	44420	57400	77070

[a] Recorded as counts/min.

The CO_2 produced in reaction (6) is instantly present when the reaction commences. Some radiochemical results are summarized in Table VI, from which it follows that a linear relation exists between the absorbance decrease at 313 nm and the count rate obtained for the released $C^{14}O_2$. Extrapolation to infinity where the absorbance is zero yields a count rate of 140,000. Experimentally an infinity value of 185,000 was recorded. This difference is ascribed to partial reduction of Au(I) to Au(0) during which additional $C^{14}O_2$ is produced.

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