

## Kinetics and Mechanism for Reduction of Tetrachloro- and Tetrabromoaurate(III) by Iodide

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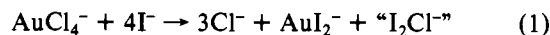
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Reduction of tetrachloro- and tetrabromoaurate(III) to gold(I) by iodide in aqueous solution has been studied by stopped-flow spectrophotometry with use of either excess iodide or excess gold(III) complex. For excess iodide, there is a single reaction, whereas for excess gold(III), reduction takes place in two consecutive steps because rapid equilibria involving the polyhalide anions  $\text{ICl}_2^-$  and  $\text{I}_2\text{Cl}^-$  influence the kinetics. Reduction by iodide is faster than ligand substitution in both  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$ , so there is no initial replacement of chloride or bromide by iodide prior to the reductive elimination. The mechanism is thus intermolecular, involving a direct attack on one of the halide ligands of the complex by an outer-sphere iodide in the rate-determining step. The observed redox kinetics is compatible with a two-step single-electron-transfer mechanism via an intermediate, which can formally be regarded as a gold(II) species, or with a two-electron-transfer mechanism. The rate constants for reduction of  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$  by iodide at 25.0 °C are  $(9 \pm 1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $(10 \pm 3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, for a 1.00 M perchlorate medium.

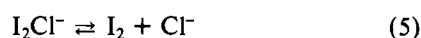
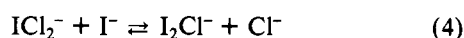
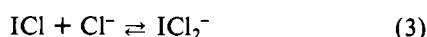
### Introduction

Tetrachloro- and tetrabromoaurate(III) complexes are rapidly reduced to gold(I) complexes by iodide in aqueous solution.<sup>1</sup> Diiodoaurate(I),  $\text{AuI}_2^-$ , is well-known.<sup>2</sup> Solid compounds containing  $\text{AuI}_4^-$  units have been prepared,<sup>3</sup> and the existence of  $\text{AuI}_4^-$  complexes in equilibrium with  $\text{AuI}_2^-$  and  $\text{I}_3^-$  in aqueous solutions saturated with iodine has been demonstrated.<sup>4</sup> We here report a study of the reaction mechanism for reduction of  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$  to gold(I) by iodide.

In the case of the tetrachloroaurate(III)-iodide system, the overall reaction for excess iodide can be written

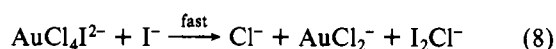


where "I<sub>2</sub>Cl<sup>-</sup>" stands for an equilibrium mixture of  $\text{I}_2\text{Cl}^-$ ,  $\text{I}_2$ , and (for large concentrations of iodide)  $\text{I}_3^-$ , described by eq 2-6. The distribution between the various halide species is



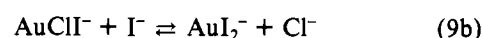
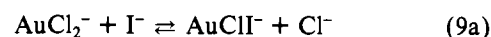
determined by the concentrations of free iodide and chloride used. The chemistry of polyhalide anions has been reviewed.<sup>5,6</sup> The equilibrium constants for reactions 2-6 are  $K_2 = 3 \times 10^{-9} \text{ M}$ ,<sup>7</sup>  $K_3 = 90 \text{ M}^{-1}$  (this work),  $K_4 = (K_2K_3)^{-1} = 3 \times 10^6$  (this work),  $K_5 = 0.57 \text{ M}$  (this work and ref 5), and  $K_6 = 710 \text{ M}^{-1}$ .<sup>7</sup>

For excess iodide and in the presence of chloride (0.1-1 M necessary to suppress aquation of  $\text{AuCl}_4^-$ ) one pseudo-first-order reaction is observed in the  $\text{AuCl}_4^-$ -iodide system. In the overall process, eq 1, 4 mol of iodide is consumed/mol of gold(III) reduced. The kinetics can be interpreted in terms of a two-step electron-transfer mechanism (eq 7 and 8) fol-



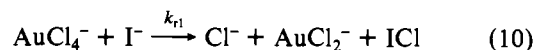
lowed by rapid ligand substitutions in the gold(I) system (eq

9). According to this model, 2 mol of iodide/mol of gold(III)



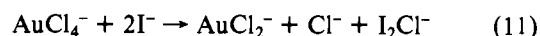
is used for reduction, whereas the other 2 mol of iodide is consumed in the consecutive fast substitutions (eq 9).

Alternatively, a two-electron-transfer process according to eq 10, followed by the rapid equilibria 9 and a rapid reaction



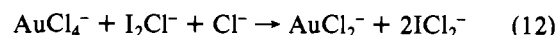
between each  $\text{ICl}$  formed and iodide to form "I<sub>2</sub>Cl<sup>-</sup>" according to the reverse of reaction 2, can be used to describe the experiments. In this case, 1 mol of iodide/mol of gold(III) is used for reduction, whereas the other 3 mol of iodide is consumed in the consecutive, fast processes.

For experiments with excess tetrachloroaurate(III), the observed kinetics is more complex, with two consecutive reactions in different time scales. In the initial rapid step only half of the added iodide is used for reduction of gold(III) according to the stoichiometric relation

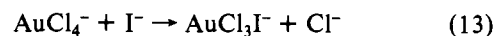


the reaction products in this case being mainly  $\text{AuCl}_2^-$  and  $\text{I}_2\text{Cl}^-$ . The kinetics and possible mechanisms for this step are identical with those for the reaction observed with excess iodide.

In the subsequent slower process there is a further reduction of gold(III) by the  $\text{I}_2\text{Cl}^-$  formed in the fast step and chloride according to the stoichiometric relation



The quantity of gold(III) reduced in this step also corresponds to half of the amount of iodide added initially. The experimental rate law for reaction 12 indicates a complicated mechanism. One report on the kinetics for the  $\text{AuCl}_4^-$ -iodide reaction has been published previously.<sup>8</sup> The observed reaction was assumed to be due to the monosubstitution



whereas redox processes were considered to be slow. That interpretation is not in accordance with the present results.

### Experimental Section

**Chemicals and Solutions.** All solutions had the ionic strength 1.00 M by addition of sodium perchlorate (Baker's p.a. recrystallized once) and perchloric acid (Baker's p.a.). Stock solutions of tetrachloro-

(1) A. K. Gangopadhyay and A. Chakravorty, *J. Chem. Phys.*, **35**, 2206 (1961).

(2) A. M. Erenburg and B. I. Peshchevskii, *Zh. Neorg. Khim.*, **14**, 932 (1969).

(3) J. L. Ryan, *Inorg. Chem.*, **8**, 2058 (1969).

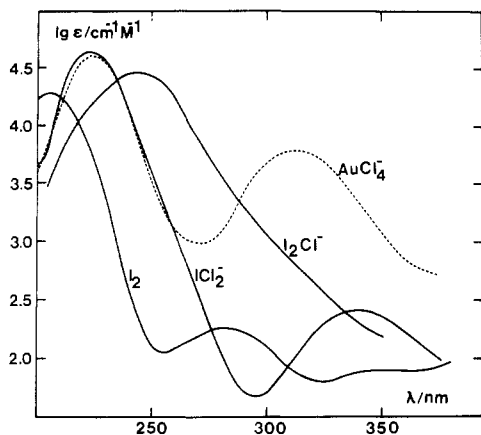
(4) Å. Håkansson and L. Johansson, *Chem. Scr.*, **7**, 201 (1975).

(5) A. I. Popov, *Halogen Chem.*, **1**, 225-260 (1967).

(6) A. J. Downs and C. J. Adams, "Comprehensive Inorganic Chemistry", Vol. 2, J. C. Bailar, Jr., Ed., Pergamon Press, Oxford, 1973, p 1534.

(7) G. Piccardi and R. Guidelli, *J. Phys. Chem.*, **72**, 2782 (1968).

(8) A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Dalton Trans.*, 1403 (1977).



**Figure 1.** Spectra of  $\text{AuCl}_4^-$ ,  $\text{I}_2\text{Cl}^-$ ,  $\text{ICl}_2^-$ , and  $\text{I}_2$ .  $\text{AuCl}_2^-$  is transparent between 200 and 500 nm.

and tetrabromoaurate(III) (2.5 mM) were prepared from  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ ,  $x \approx 3$  (Degussa). To suppress hydrolysis, they also contained sodium chloride (100 mM) and sodium bromide (25 mM), respectively (Merck Suprapur). Absorption spectra agreed with previously reported spectra<sup>9</sup> for  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$ .

Stock solutions of iodide (1 mM) were prepared from a 1.00 M solution of sodium iodide (Merck Suprapur) and 1.00 M sodium perchlorate. Solutions were kept in a refrigerator in the dark and were flushed with nitrogen to avoid oxidation. A stock solution of  $\text{ICl}_2^-$  (8.4 mM) in 1.00 M sodium chloride was prepared by melting  $\text{ICl}$  (Merck zur Synthese, mp 28 °C) on a water bath at 35 °C and transferring a droplet (137.8 mg) to a weighed 100-mL volumetric flask filled with a nitrogen-flushed solution of sodium chloride (0.99 M) and hydrochloric acid (10 mM). After transfer, the flask was weighed, wrapped in a foil, and placed on a magnetic stirrer at 40 °C, and nitrogen was passed over the solution. After less than 1 h, all  $\text{ICl}$  had dissolved. For the 1 M chloride concentration used, the predominant species was  $\text{ICl}_2^-$ . Hydrolysis is negligible,<sup>10</sup> and the spectrum (see Figure 1), which agreed with that in the literature,<sup>11</sup> showed that the solution was stable for several days.

An iodine stock solution ( $7.32 \times 10^{-4}$  M) was prepared by dissolution of a weighed amount (55.74 mg) of iodine (Merck doppelt sublimiert, small particles) in 300 mL of nitrogen-flushed sodium perchlorate solution (1.00 M). Nitrogen was passed over the surface, and the flask was wrapped in a foil. After 15 h on a magnetic stirrer, all iodine had dissolved. The spectrum shown in Figure 1 agrees with that in the literature.<sup>12</sup> The solution was stable for several months, if kept in the dark under nitrogen. The  $\text{I}_2\text{Cl}^-$  solutions used in the kinetic experiments were prepared by mixing 5 mL of iodine stock solution with 100 mL of sodium chloride solution (1.00 M) in a 200-mL volumetric flask (nitrogen flushed), which was then filled with sodium perchlorate solution (1.00 M). A slow decrease of the absorbance peak at 243 nm (cf. Figure 1) indicated a slow decomposition during a period of some days. Therefore, all solutions used were freshly prepared.

**Apparatus.** Spectra were recorded by using Cary 14 and Beckman 25 recording spectrophotometers. The stopped-flow instrument was the same as described previously.<sup>13</sup>

**Gold(I) Spectra and Equilibria.** To 100 mL of a tetrachloroaurate(III) solution ( $C_{\text{Au}} = 1 \times 10^{-4}$  M,  $C_{\text{NaCl}} = C_{\text{NaClO}_4} = 0.50$  M) was added an equivalent amount of sulfite (2.0 mL of 5 mM  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ , Merck p.a.). Reduction was complete within 1 h. The solution is stable for several hours.<sup>2</sup> The products are  $\text{AuCl}_2^-$  and sulfate, but the high chloride concentration is likely to suppress formation of any sulfato complexes. The spectrum of the solution has no absorption bands between 500 and 200 nm. Spectra of solutions having a gold(I) concentration of  $4 \times 10^{-6}$  M (prepared from the solution described above) and iodide concentrations of 0.4, 2, 4, and 6  $\mu\text{M}$  and with sodium chloride (0.50 M) were also recorded. There

**Table I.** Observed Rate Constants for Reduction of  $\text{AuCl}_4^-$  by Iodide at 25.0 °C<sup>a</sup>

$C_{\text{Cl}^-}/\text{M}$	$10^4 C_{\text{I}^-}/\text{M}$	$10^6 C_{\text{Au}^+}/\text{M}$	$k_{\text{exptl}}^b/s^{-1}$	$\lambda/\text{nm}$
Excess Iodide				
0.500	1.19	6.36	8.8	260 or 315
	1.99		16.6	
	2.98		24.0	
	3.97		32.5	
	4.96		41.5	
0.500	1.19	3.18	9.5	260
	1.99		15.4	
	2.98		24.0	
	3.97		32.2	
	4.96		41.6	
0.0100	1.49	6.36	10.5 <sup>c</sup>	260 or 315
0.100	1.49		11.9 <sup>c</sup>	
0.300	1.49		12.1 <sup>c</sup>	
0.850	1.49		12.8 <sup>c</sup>	
Excess Complex, Rapid Reaction				
0.500	0.025	25.4	4.0	315
		50.8	5.6	
		76.0	8.2	
		102	18.5	
0.500	0.025	127	14.3	260
		25.4	5.4	
		50.8	10.0	
		76.2	20.2	
		102	24.2	
0.500 <sup>d</sup>	0.0993	127	27.2	260
		254	42.7	
		381	55.6	
		508	63.3	

<sup>a</sup> The ionic medium was 1.00 M sodium perchlorate, and the hydrogen ion concentration was  $5 \times 10^{-3}$  M when not otherwise stated. <sup>b</sup> Mean values given. <sup>c</sup>  $[\text{H}^+] = 0.1$  M in these experiments in order to suppress hydrolysis of  $\text{AuCl}_4^-$ . <sup>d</sup> In these four experiments the subsequent process was also monitored; cf. Table III.

is an absorption maximum at 223 nm, which increases linearly with the iodide concentration and which has a molar absorptivity (per mole of iodide) of  $1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ . Both the position of the band and its molar absorptivity indicate that it is due to free iodide.<sup>14</sup> Thus, complex formation according to eq 9 is probably insignificant in these solutions. For larger concentrations of gold(I) ( $4 \times 10^{-5}$  M) and iodide ( $2 \times 10^{-5}$  M) there is an immediate precipitation of  $\text{AuI}(s)$ .

**Polyhalide Spectra and Equilibria.** The spectrum of  $\text{ICl}_2^-$  shown in Figure 1 was recorded by using  $8.4 \times 10^{-6}$  and  $4.2 \times 10^{-3}$  M solutions containing 1.00 M sodium chloride to displace equilibrium 3 to the right. There is a strong band at 223 nm with a molar absorptivity of  $4.3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$  and a weaker one at 340 nm ( $2.6 \times 10^2 \text{ cm}^{-1} \text{ M}^{-1}$ ). The spectrum agrees rather well with that in the literature.<sup>11,15</sup> The equilibrium constant  $K_3 = [\text{ICl}_2^-]/([\text{ICl}][\text{Cl}^-])$  for reaction 3 was calculated from the absorbance at the 223-nm peak of three solutions with varying chloride concentrations,  $C_{\text{Cl}^-}$  (1.00 mM, 11.0 mM, and 1.00 M), and a constant concentration of  $\text{ICl}_2^-$ ,  $C_{\text{ICl}_2^-} = [\text{ICl}_2^-] + [\text{ICl}] = 8.4 \times 10^{-6}$  M ( $\ll C_{\text{Cl}^-}$ ). The absorptivities,  $\epsilon = \epsilon_{\text{ICl}}[\text{ICl}] + \epsilon_{\text{ICl}_2^-}[\text{ICl}_2^-]$ , were 0.026, 0.179, and  $0.354 \text{ cm}^{-1}$ , respectively, which gave  $K_3 = 90 \text{ M}^{-1}$  if  $\epsilon_{\text{ICl}} \ll \epsilon_{\text{ICl}_2^-}$  at the wavelength used. There is a previous value for  $K_3$  of  $160 \pm 30 \text{ M}^{-1}$ .<sup>16</sup> Hydrolysis of  $\text{ICl}$  in these solutions is very slow and was suppressed by addition of hydrochloric or perchloric acid (0.100 M).<sup>10</sup> The value of  $K_3$  implies that  $[\text{ICl}_2^-] \gg [\text{ICl}]$  for the chloride concentrations used in the kinetics measurements (cf. Tables I and III).

The spectrum of  $\text{I}_2\text{Cl}^-$  and the equilibrium constant for reaction 5 were calculated from the spectra of three solutions, which were mixed from iodine, sodium chloride, and sodium perchlorate stock solutions.

(9) L. I. Elding and A.-B. Grönig, *Acta Chem. Scand., Ser. A*, **A32**, 867 (1978).

(10) H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 2031 (1932).

(11) D. L. Cason and H. M. Neumann, *J. Am. Chem. Soc.*, **83**, 1822 (1961).

(12) A. D. Awtry and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).

(13) L. I. Elding and L. F. Olsson, *Inorg. Chem.*, **16**, 2789 (1977).

(14) E. Lederle, *Z. Phys. Chem., Abt. B*, **10**, 121 (1930).

(15) R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 4845 (1954).

(16) J. H. Faull, *J. Am. Chem. Soc.*, **56**, 523 (1934).

Table II. Observed Rate Constants for Reduction of AuBr<sub>4</sub><sup>-</sup> by Iodide<sup>a</sup>

<i>t</i> /°C	10 <sup>3</sup> <i>C</i> <sub>I</sub> /M	<i>k</i> <sub>exptl</sub> <sup>b</sup> /s <sup>-1</sup>
24.9	1.0	82
	1.5	147
	2.0	196
	2.5	214
15.8	1.0	67
	1.5	103
	2.0	157
	2.5	222
	3.0	226
3.8	1.0	58
	1.5	58
	2.0	82
	2.5	114
	3.0	134

<sup>a</sup> The total concentrations were *C*<sub>Br</sub> = 5 × 10<sup>-3</sup> M, [H<sup>+</sup>] = 5 × 10<sup>-3</sup> M, and *C*<sub>Au</sub> = 1.27 × 10<sup>-6</sup> M and the wavelength was 255 nm.  
<sup>b</sup> Mean values given.

The total concentration of iodine, *C*<sub>I<sub>2</sub></sub> = [I<sub>2</sub>] + [I<sub>2</sub>Cl<sup>-</sup>], was 2.20 × 10<sup>-3</sup> M (<<*C*<sub>Cl</sub>), and the chloride concentration, *C*<sub>Cl</sub>, was varied (10.0 mM, 100 mM, 1.00 M). From the absorptivities at 243 nm, *e* = ε<sub>I<sub>2</sub></sub>[I<sub>2</sub>] + ε<sub>I<sub>2</sub>Cl<sup>-</sup></sub>[I<sub>2</sub>Cl<sup>-</sup>] (0.015, 0.200, and 0.807 cm<sup>-1</sup>, respectively) and ε<sub>I<sub>2</sub></sub> = 390 cm<sup>-1</sup> M<sup>-1</sup>, *K*<sub>5</sub> = [I<sub>2</sub>][Cl<sup>-</sup>]/[I<sub>2</sub>Cl<sup>-</sup>] was obtained as 0.57 M, in good agreement with the literature.<sup>5</sup> Thus, for the kinetics experiments with 0.50 M chloride (Tables I and III), the concentration ratio is [I<sub>2</sub>Cl<sup>-</sup>]/[I<sub>2</sub>] = 0.87. The spectrum of I<sub>2</sub>Cl<sup>-</sup> shown in Figure 1 was calculated from the I<sub>2</sub> spectrum in Figure 1 and the equilibrium constant from the I<sub>2</sub> spectrum in Figure 1 and the equilibrium constant *K*<sub>5</sub>. I<sub>2</sub>Cl<sup>-</sup> has a band at 243 nm with ε = 2.9 × 10<sup>4</sup> cm<sup>-1</sup> M<sup>-1</sup>. There seems to be agreement in the literature that there is an absorbance maximum between 245 and 250 nm, but the molar absorptivities reported scatter between 1 × 10<sup>4</sup> and 5.5 × 10<sup>4</sup> cm<sup>-1</sup> M<sup>-1</sup>.<sup>11,17</sup>

The equilibrium constant for reaction 4, *K*<sub>4</sub> = [I<sub>2</sub>Cl<sup>-</sup>][Cl<sup>-</sup>]/([ICl<sub>2</sub><sup>-</sup>][I<sup>-</sup>]), was calculated by iteration from the absorbance at 243 and 223 nm of a solution with *C*<sub>Cl</sub> = 1.92 M and *C*<sub>I<sub>2</sub></sub> = 2.9 × 10<sup>-6</sup> M by using the known molar absorptivities of I<sub>2</sub>Cl<sup>-</sup>, ICl<sub>2</sub><sup>-</sup>, and I<sup>-</sup>. *K*<sub>4</sub> = 3 × 10<sup>6</sup> was obtained, in good agreement with (*K*<sub>2</sub>*K*<sub>3</sub>)<sup>-1</sup>.

**Kinetics.** Pseudo-first-order rate constants were calculated from experiments with either excess iodide or excess gold(III) complex. For excess iodide (Tables I and II) only one reaction could be observed, at all wavelengths. For excess AuCl<sub>4</sub><sup>-</sup>, there is one fast increase of absorbance at 260 nm, followed by an equally large slow decrease. The spectra in Figure 1 show that at 260 nm, the molar absorptivities for AuCl<sub>4</sub><sup>-</sup> and ICl<sub>2</sub><sup>-</sup> are equal, about 10<sup>3</sup> cm<sup>-1</sup> M<sup>-1</sup>, whereas that of I<sub>2</sub> is negligible. The observed change can therefore be described as a formation of I<sub>2</sub>Cl<sup>-</sup> in the first step, followed by a disappearance of this species in the subsequent step.

The slow subsequent reaction could be carefully monitored by delaying the start of the oscilloscope sweep until the fast reaction was complete (Table III, subsequent reaction). It could also be followed directly by mixing AuCl<sub>4</sub><sup>-</sup> solutions with solutions of I<sub>2</sub>Cl<sup>-</sup> (Table III, direct reaction). The chloride system was studied at 25.0 °C only, whereas the much faster AuBr<sub>4</sub><sup>-</sup>-iodide reaction was monitored at 3.8, 15.8, and 25.0 °C and 255 nm (Table II).

In the experiments with excess AuCl<sub>4</sub><sup>-</sup>, both solutions mixed in the stopped-flow instrument had the same concentrations of chloride. Thus, there was no shift in the I<sub>2</sub>Cl<sup>-</sup>/I<sub>2</sub> equilibrium (eq 5). In the experiments with excess iodide, one of the drive syringes contained sodium iodide and the other gold(III) complex with chloride or bromide in excess.

The polyhalide reactions (2)–(6) are fast on the stopped-flow time scale. For instance, the triiodide formation rate constant according to reaction 6 is 4 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>18</sup> Only reaction 4 could be qualitatively followed by using second-order conditions and very low initial concentrations ([I<sup>-</sup>] = [ICl<sub>2</sub><sup>-</sup>] = 2.5 × 10<sup>-6</sup> M; [Cl<sup>-</sup>] = 0.50 M after mixing). As expected, the absorbance decreased at 223 nm and increased at 250 nm; compare Figure 1. The reaction was

Table III. Observed Rate Constants for the Slow Process<sup>a</sup>

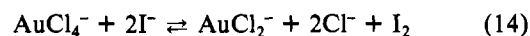
initial reductant	<i>C</i> <sub>Cl</sub> /M	10 <sup>4</sup> × <i>C</i> <sub>Au</sub> /M	10 × <i>k</i> <sub>exptl</sub> <sup>b</sup> /s <sup>-1</sup>
Subsequent Reaction <sup>c</sup>			
<i>C</i> <sub>Au</sub> > <i>C</i> <sub>I</sub> = 9.93 × 10 <sup>-6</sup> M	0.50	1.27	2.0
		2.54	4.1
		3.81	6.0
		5.08	7.6
Direct Reaction			
<i>C</i> <sub>Au</sub> > <i>C</i> <sub>I<sub>2</sub></sub> <sup>d</sup> = 9.15 × 10 <sup>-6</sup> M, <i>C</i> <sub>I</sub> = 0	0.50	0.95	1.2
		1.27	1.5
		1.90	2.5
		2.54	3.3
Direct Reaction			
<i>C</i> <sub>I<sub>2</sub></sub> = 1.39 × 10 <sup>-5</sup> M	0.130	3.81	0.57
		0.200	0.94
		0.265	1.43
<i>C</i> <sub>I<sub>2</sub></sub> = 1.23 × 10 <sup>-5</sup> M	0.500	1.02	1.33
		0.200	0.79
		0.300	1.06
<i>C</i> <sub>I<sub>2</sub></sub> = 1.13 × 10 <sup>-5</sup> M	0.500	1.02	1.23
		0.200	0.84
		0.265	1.19
<i>C</i> <sub>I<sub>2</sub></sub> = 8.2 × 10 <sup>-6</sup> M	0.500	1.02	1.38
		0.800	1.90

<sup>a</sup> Wavelength 260 nm; 25 °C, 1 M perchlorate medium. <sup>b</sup> Mean values given. <sup>c</sup> Compare with experiments in Table I; see footnote d. <sup>d</sup> *C*<sub>I<sub>2</sub></sub> = [I<sub>2</sub>] + [I<sub>2</sub>Cl<sup>-</sup>].

complete within 100 ms, which means that the rate constant is about 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>, if complete conversion to I<sub>2</sub>Cl<sup>-</sup> is assumed. The equilibrium constant *K*<sub>4</sub> gives the rate constant for the reverse of reaction 4 as approximately 3 M<sup>-1</sup> s<sup>-1</sup>.

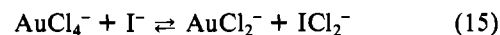
## Results and Discussion

**Stoichiometry.** The standard electrode potential for I<sub>2</sub>/I<sup>-</sup> is 0.615 V for a 0.1 M chloride medium,<sup>19</sup> and that for AuCl<sub>4</sub><sup>-</sup>/AuCl<sub>2</sub><sup>-</sup> can be calculated to be 0.929 V from literature data<sup>20</sup> for AuCl<sub>2</sub><sup>-</sup>/Au (1.154 V) and AuCl<sub>4</sub><sup>-</sup>/Au (1.002 V). For low concentrations of chloride the reduction of AuCl<sub>4</sub><sup>-</sup> by iodide can be written



with *E*<sup>o</sup> = 0.311 V, corresponding to *K*<sub>14</sub> = 3 × 10<sup>10</sup> M. For larger chloride concentrations I<sub>2</sub>Cl<sup>-</sup> will be the main reaction product according to reaction 11. The equilibrium constant for reaction 11 is *K*<sub>11</sub> = *K*<sub>14</sub>/*K*<sub>5</sub> = 3 × 10<sup>10</sup>/0.57 = 6 × 10<sup>10</sup>. Thus, for excess iodide, reduction according to both eq 14 and 11 is complete.

For smaller concentrations of iodide, the main process is

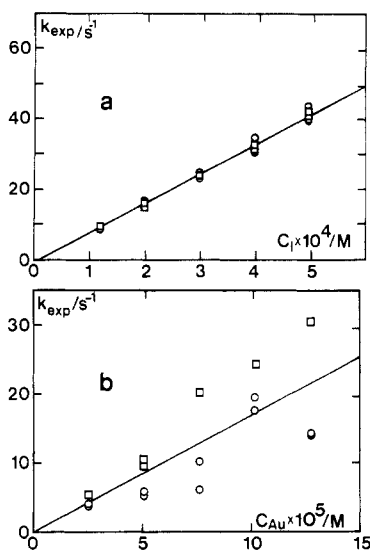


with *K*<sub>15</sub> = *K*<sub>11</sub>/*K*<sub>4</sub> = 6 × 10<sup>10</sup>/(3 × 10<sup>6</sup>) = 2 × 10<sup>4</sup>. In this case also, reduction is practically complete for the concentrations used. Accordingly, the spectrum between 360 and 260 nm of a solution with *C*<sub>I</sub> ≤ *C*<sub>Au</sub> ≈ 1 × 10<sup>-5</sup> M and *C*<sub>Cl</sub> = 0.90 M indicates complete reduction.

In the experiments with excess tetrachloroaurate(III) summarized in Table III, we must also consider reduction according to eq 12. The equilibrium constant is *K*<sub>12</sub> = *K*<sub>15</sub>/*K*<sub>4</sub> = 2 × 10<sup>4</sup>/(3 × 10<sup>6</sup>) ≈ 1 × 10<sup>-2</sup>, which indicates that in this case also, reduction is complete for the concentrations used.

(17) D. Meyerstein and A. Trenin, *Trans. Faraday Soc.*, **59**, 1114 (1963).  
(18) O. E. Myers, *J. Chem. Phys.*, **28**, 1027 (1958).

(19) G. Milazzo and S. Caroli, "Tables of Standard Electrode Potentials", Project of the IUPAC Electrochemistry Commission, Wiley, New York, 1978, p 292.  
(20) L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand., Ser. A*, **A31**, 155 (1977).



**Figure 2.** Reduction of tetrachloroaurate(III) by iodide. (a) Excess iodide. The observed rate constant is plotted vs.  $C_I$ . The total concentration of complex was  $6.36 \times 10^{-6}$  (O) and  $3.18 \times 10^{-6}$  M ( $\square$ ). (b) Excess tetrachloroaurate(III). The observed rate constant for the rapid initial process is plotted vs.  $C_{\text{Au}}$  at 260 ( $\square$ ) and 315 nm (O). The total concentration of iodide was  $2.5 \times 10^{-6}$  M.

This was confirmed by the spectrum between 350 and 200 nm of a solution with  $C_I \leq C_{\text{Au}} \approx 1 \times 10^{-5}$  M and  $C_{\text{Cl}} = 0.50$  M.

The magnitude of the absorbance changes in the kinetics runs also gives information about the stoichiometry. At 260 nm, the change in absorptivity per molar unit of  $\text{AuCl}_4^-$  in the experiments with excess iodide is twice the change per molar unit of iodide observed for the rapid reaction when  $\text{AuCl}_4^-$  is in excess. This is compatible with a model where 1 mol of  $\text{I}_2\text{Cl}^-$ /mol of  $\text{AuCl}_4^-$  is formed in the single reaction observed when excess iodide is used according to reaction 1. For excess  $\text{AuCl}_4^-$ , on the other hand, only 0.5 mol of  $\text{I}_2\text{Cl}^-$  is formed/initial mol of iodide in the rapid reaction step, in accordance with reaction 11. The absorbance change for the slow subsequent step indicates that the  $\text{I}_2\text{Cl}^-$  formed in the rapid step disappears completely in a further reduction according to eq 12.

**Rate Laws. Excess Iodide.** For excess iodide, we follow the disappearance of  $\text{AuCl}_4^-$  and formation of an equilibrium mixture of  $\text{I}_2\text{Cl}^-$ ,  $\text{I}_2$ , and  $\text{I}_3^-$  according to reaction 1. The absorbance at 260 nm increases and that at 315 nm decreases; compare spectra in Figure 1. With reaction 7 rate determining and reactions 8, 9, and 2–6 rapid, or with reaction 10 rate determining and reactions 9 and 2–6 rapid, we have the simple rate law

$$-d[\text{AuCl}_4^-]/dt = k_{r1}[\text{I}^-][\text{AuCl}_4^-] = k_{\text{exptl}}[\text{AuCl}_4^-] \quad (16)$$

Figure 2a shows a plot of the observed rate constant as a function of iodide concentration. The experiments at the two wavelengths agree. The slope of the plot in Figure 2a gives  $k_{r1} = (8.5 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . It should be noted that—contrary to the previous report by Hall and Satchell<sup>8</sup>—the rate is independent of chloride concentration; see Table I.

The results for the  $\text{AuBr}_4^-$ -iodide reaction given in Table II also agree with a rate law analogous to eq 16, but because of the rapid kinetics, the experimental scatter is much larger in this case. Approximate  $k_{r1}$  constants are given in Table IV. The activation energy for the reduction of  $\text{AuBr}_4^-$  by iodide is approximately  $30 \pm 5$  kJ/mol.

**Excess Complex, Rapid Reaction.** For excess gold and with iodide as the initial reductant, there are two reactions. The increase of absorbance at 260 nm for the rapid initial process corresponds to formation of 0.5 mol of “ $\text{I}_2\text{Cl}^-$ ” equilibrium

**Table IV.** Rate Constants for Reduction of  $\text{AuCl}_4^-$  and  $\text{AuBr}_4^-$  by Iodide in a 1.00 M Sodium Perchlorate Medium

complex	$t/^\circ\text{C}$	$k_{r1}/\text{M}^{-1} \text{ s}^{-1}$
$\text{AuCl}_4^-$	25.0	$(8.5 \pm 0.3) \times 10^4$ <sup>a</sup> $(9 \pm 2) \times 10^4$ <sup>b</sup>
$\text{AuBr}_4^-$	3.8	$(4 \pm 2) \times 10^6$ <sup>a</sup>
	15.8	$(9 \pm 3) \times 10^6$ <sup>a</sup>
	25.0	$(10 \pm 3) \times 10^6$ <sup>a</sup>

<sup>a</sup>  $C_{\text{Au}} \ll C_{\text{I}}$ . <sup>b</sup>  $C_{\text{Au}} \gg C_{\text{I}}$ .

mixture/mol of iodide originally present. For the small concentrations of free iodide used in these experiments (less than  $10^{-7}$  M after reduction; see Table I),  $\text{ICl}_2^-$  is the thermodynamically stable species. However,  $\text{I}_2\text{Cl}^-$  is formed initially as a metastable intermediate, because the rate of reduction (the reduction rate constant  $2k_{r1}[\text{AuCl}_4^-]$  varies between ca. 5 and  $65 \text{ s}^{-1}$ ) is always larger than the rate of formation of the thermodynamically stable  $\text{ICl}_2^-$  according to the reverse of reaction 4 (rate constant  $3 \times [\text{Cl}^-]$  ca.  $1 \text{ s}^{-1}$ ).

Thus, for each mol of gold(III) reduced, 2 mol of iodide is consumed. With reaction 7 rate determining and reaction 8 rapid, the rate law is given by eq 18. Alternatively, with reaction 10 rate determining and reactions 2–5 rapid, the iodide is simultaneously consumed via reaction 10 and the reverse of reaction 2. We then arrive at

$$-d[\text{I}^-]/dt = 2\{d([\text{I}_2\text{Cl}^-] + [\text{I}_2])/dt\} = -2\{d[\text{AuCl}_4^-]/dt\} \quad (17)$$

which gives

$$-d[\text{I}^-]/dt = 2k_{r1}[\text{AuCl}_4^-][\text{I}^-] = k_{\text{exptl}}[\text{I}^-] \quad (18)$$

Figure 2b shows a plot of the experimental values in Table I according to eq 18. The scatter is rather large, because the infinity values are disturbed by the subsequent process in these experiments. However, the slope ( $2k_{r1}$ ) gives  $k_{r1} = (9 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , which agrees satisfactorily with the value calculated from the experiments using excess iodide; cf. Table IV. Thus, the rapid initial process can be interpreted as a reduction of tetrachloroaurate(III) by half of the amount of added iodide.

**Intimate Mechanism for Reduction with Iodide.** The spectral changes between 220 and 370 nm for the single reaction observed when excess iodide is used are compatible with a change from  $\text{AuCl}_4^-$  to  $\text{I}_2\text{Cl}^-$  as the dominant absorbing species; compare the spectra in Figure 1. For instance, isosbestic points can be observed at 235 and 290 nm for this reaction. The overall process can therefore be written as eq 1, and a rapid chloride-iodide substitution in  $\text{AuCl}_4^-$  followed by a rate-determining reduction can be excluded.

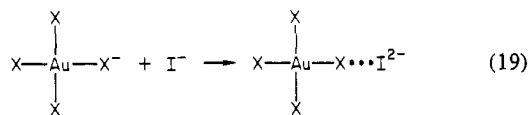
The possibility of a rate-determining ligand substitution followed by a rapid reduction also seems less likely. If we consider the rate constants for the monosubstitution of a chloride in  $\text{AuCl}_4^-$  by radiochloride ( $1.5 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>21</sup> bromide ( $63 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>9</sup> and thiocyanate ( $1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>22</sup> and of a bromide in  $\text{AuBr}_4^-$  by chloride ( $10.7 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>9</sup> and thiocyanate ( $8.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>22</sup> and remember that iodide and thiocyanate are rather similar as entering ligands, it is not very likely that the rate constants for substitution of a halide by iodide in  $\text{AuCl}_4^-$  and—especially—in  $\text{AuBr}_4^-$  are as large as the observed values of  $9 \times 10^4$  and  $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

An intermolecular mechanism therefore seems likely, the first step being a direct attack on a chloride or bromide ligand

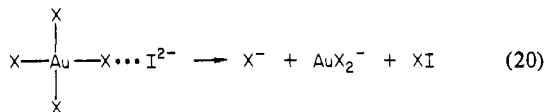
(21) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 57 (1954).

(22) L. I. Elding, A.-B. Gröning, and Ö. Gröning, *J. Chem. Soc., Dalton Trans.*, 1093 (1981).

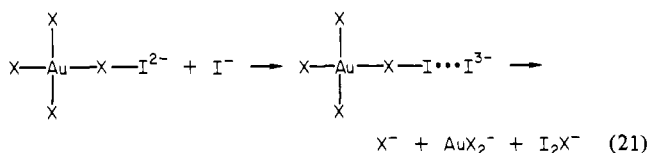
of the complex by an outer-sphere iodide, without any prior substitution:



The reaction might proceed either by a direct two-electron transfer and formation of gold(I) and IX (cf. the mechanisms previously suggested to describe square-planar  $\leftrightarrow$  octahedral redox reactions<sup>23-27</sup>) according to eq 20 or by two consecutive

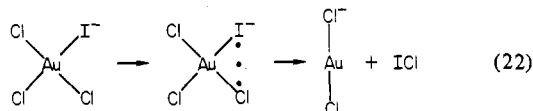


one-electron transfers. In the latter case,  $\text{AuX}_4\text{I}^{2-}$  must be considered as an intermediate (formally gold(II)), which can be further reduced by a second iodide in a fast subsequent step (eq 21). According to these models, the difference in rate



of reduction by a factor of 100 between the bromide and chloride complex is explained by bromide being a more efficient bridging ligand than chloride.

Pearson<sup>28</sup> has discussed an alternative mechanism for linear  $\leftrightarrow$  square-planar redox reactions. As applied to the present process, it should involve a rapid initial ligand substitution, in which  $\text{AuCl}_3\text{I}^-$  is formed according to eq 13. The reaction proceeds via an  $E_u$  bending motion, so that the halogen molecule  $\text{ICl}$  is formed from an iodide and a chloride ligand cis to each other (eq 22). In addition to the fact that there



probably is not any rapid initial monosubstitution, mechanism 22 involves a rather extreme rearrangement of the ligands of the complex. Moreover, the reverse process (i.e., the oxidative cis addition) has a rather high energy barrier, because one filled d orbital of the linear complex has its lobe in the I-Cl bond and therefore will be raised in energy.<sup>28</sup> As applied to the reductive elimination, this means that the  $E_u$  bending (cf. ref 28, p 183) involved in eq 22 must be strongly activated; it is hardly possible for the ground-state  $\text{AuCl}_3\text{I}^-$  to react in this manner. It should also be noted in this context that the intermolecular mechanism proposed by Ford-Smith and co-workers<sup>29</sup> for the oxidation of  $\text{Au}(\text{CN})_2^-$  by iodine, which involves oxidative trans addition, is not symmetry allowed.<sup>28</sup>

Mechanisms 22 and 19-21 might also be compared in terms of the symmetry of the atomic motions and electronic wave

(23) G. Dolcetti, A. Peloso, and M. L. Tobe, *J. Chem. Soc.*, 5196 (1965).

(24) A. Peloso, *Coord. Chem. Rev.*, 10, 123 (1973), and references therein.

(25) A. J. Poë and D. H. Vaughan, *J. Am. Chem. Soc.*, 92, 7537 (1970), and references therein.

(26) L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 19, 165 (1976), and references therein.

(27) R. J. Mureinik and E. Pross, *J. Coord. Chem.*, 8, 127 (1978).

(28) R. G. Pearson, "Symmetry Rules for Chemical Reactions", Wiley, New York, 1976, pp 286-287.

(29) M. H. Ford-Smith, J. J. Habeeb, and J. H. Rawsthorne, *J. Chem. Soc., Dalton Trans.*, 2116 (1972).

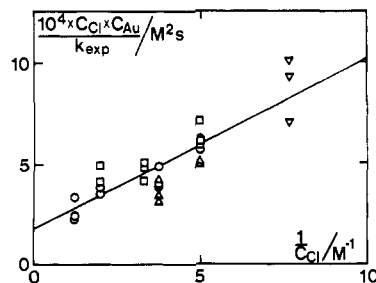


Figure 3. Plot of  $C_{\text{Cl}}C_{\text{Au}}/k_{\text{exptl}}$  vs.  $1/C_{\text{Cl}}$  for the slow subsequent process; compare eq 26. The total concentration of  $\text{I}_2\text{Cl}^-$  was  $8.2 \times 10^{-6}$  (O),  $1.13 \times 10^{-5}$  (□),  $1.23 \times 10^{-5}$  (Δ), and  $1.39 \times 10^{-5}$  M (▽).

functions. The electron density and its change can be expressed as

$$\rho = \rho_0 + 2 \frac{\langle \psi_0 | \delta U / \delta Q | \psi_k \rangle}{E_0 - E_k} \psi_0 \psi_k Q \quad (23)$$

(notation, ref 28, pp 13 and 24). The second term of eq 23 contains the gradient of the electron density along the  $Q$  coordinate.

Thus the product

$$2 \frac{\langle \psi_0 | \delta U / \delta Q | \psi_k \rangle}{E_0 - E_k} \psi_0 \psi_k Q = Q \text{ grad}_Q \rho$$

is the scalar product of the vectors  $Q$  and  $\text{grad}_Q \rho$ . Bond breaking and bond making correspond to changes in electron density, i.e., to  $\text{grad}_Q \rho$ . The scalar product will be zero (i.e., no coupling between atomic motions and bond changes) except when the two vectors are of the same symmetry species and nonperpendicular. According to mechanism 22 bond making between the two cis ligands coincides very nearly with the  $E_u$  bending motion, whereas bond breaking between gold and leaving halogen is perpendicular to it. Thus, only bond making but not breaking is coupled to the  $E_u$  bending. This is contrary to mechanisms 19 and 21, where all bond changes fall in the same direction as one of the components of the  $E_u$  stretch, if the conformations of  $\text{X}-\text{Au}-\text{X}-\text{I}$  and  $\text{X}-\text{Au}-\text{X}-\text{I}-\text{I}$  are supposed to be linear.

**Excess Complex, Slow Reaction.** The slow subsequent process is accompanied by a decrease of the absorbance at 260 nm, equal in magnitude to the initial rapid increase and corresponding to a disappearance of the " $\text{I}_2\text{Cl}^-$ " equilibrium mixture formed in the rapid step. The experiments both with  $\text{I}^-$  and with  $\text{I}_2\text{Cl}^-$  as initial reductants are summarized in Table III. The experimental values show that the reaction is first order with respect to tetrachloroaurate(III) and that the processes observed when either iodide or  $\text{I}_2\text{Cl}^-$  is used as the initial reductant are identical. Rate constants were calculated with assumption of a first-order dependence with respect to  $\text{I}_2\text{Cl}^-$ . For excess tetrachloroaurate(III) and chloride we get

$$-d([\text{I}_2\text{Cl}^-] + [\text{I}_2])/dt = k_{\text{exptl}}[\text{I}_2\text{Cl}^-] \quad (24)$$

The variation of the observed rate constant with the concentration of complex and chloride (cf. Table III) might be expressed as

$$k_{\text{exptl}} = K[\text{Cl}^-][\text{AuCl}_4^-]/(1 + K''/[\text{Cl}^-]) \quad (25)$$

which can be rearranged to the linear relation

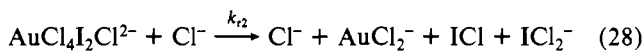
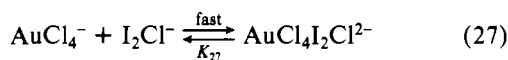
$$[\text{Cl}^-][\text{AuCl}_4^-]/k_{\text{exptl}} = 1/K' + K''/(K'[\text{Cl}^-]) \quad (26)$$

The plot in Figure 3 gives  $K' = (6 \pm 1) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$  and  $K'' = 0.51 \pm 0.05 \text{ M}$ .

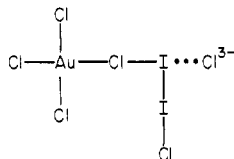
**Mechanism for the Slow Reaction.** The first-order dependence on gold(III), eq 25, excludes directly a mechanism in which iodide is formed from  $\text{I}_2\text{Cl}^-$  according to the reverse of

reaction 4 as a rate-determining step, followed by a fast reduction of  $\text{AuCl}_4^-$  by iodide.

The value of  $K''$  obtained from the kinetics agrees rather well with the equilibrium constant  $K_5 = 0.57$  M, which might indicate that reaction 5 is involved as a fast preequilibrium. One possible mechanism compatible with the rate law, eq 24 and 25, is a rapid equilibrium according to eq 5 followed by eq 27 and 28. Here, the species formed in the hypothetical

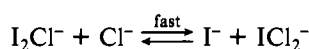
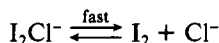


rapid equilibrium (27) is reduced in the rate-determining step, eq 28, for instance via an attack by chloride on one of the iodides of the  $\text{I}_2\text{Cl}^-$  unit:

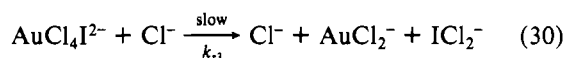
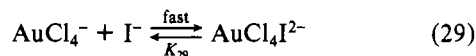


In this case, the parameter  $K'$  of eq 25 should be identified with the product  $K_{27}k_{r2}$ . The experimental value,  $6 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$ , gives no hint as to the probability of this mechanism, since neither  $K_{27}$  nor  $k_{r2}$  is known.

We have also considered the possibility that the rate-determining step for the slow reaction is the same as for the fast one, i.e., a direct reduction of the gold complex by free halide. In that case it is necessary to postulate that reaction 5 and the reverse of reaction 4 are involved as rapid preequilibria:<sup>30</sup>



which are followed by reactions 29 and 30 which are analogous



to reactions 7 and 8. This mechanism leads to rate expression 31, where  $C_1$  denotes the total concentration of iodide. In the

$$\frac{d[\text{ICl}_2^-]}{dt} = \frac{K_{29}k_{r3}K_4^{-1}[\text{Cl}^-]^2[\text{AuCl}_4^-]}{2(1 + K_5/[\text{Cl}^-])[\text{ICl}_2^-] + [\text{Cl}^-]/K_4} (C_1 - [\text{ICl}_2^-]) \quad (31)$$

denominator of eq 31,  $[\text{Cl}^-]/K_4$  is small compared to the other term, so the equation might be simplified to

$$d[\text{ICl}_2^-]/dt = k'(C_1 - [\text{ICl}_2^-])/[\text{ICl}_2^-] \quad (32)$$

(30) That reaction 4 is rapid on the time scale of the subsequent slow reaction follows from the kinetic experiment described in the Experimental Section and the value of  $K_4$ .

where the rate constant  $k'$  is given by

$$k' = \frac{1}{2}K_{29}k_{r3}K_4^{-1}[\text{Cl}^-]^2[\text{AuCl}_4^-]/(1 + K_5/[\text{Cl}^-]) \quad (33)$$

Integration of eq 32, however, leads to rate expression 34,

$$\ln([\text{ICl}_2^-]_{\text{eq}} - [\text{ICl}_2^-]) = \ln([\text{ICl}_2^-]_{\text{eq}} - [\text{ICl}_2^-]_0) - tk'/([\text{ICl}_2^-]_{\text{eq}} - ([\text{ICl}_2^-] - [\text{ICl}_2^-]_0)/[\text{ICl}_2^-]_{\text{eq}}) \quad (34)$$

which is not strictly first order with respect to  $\text{ICl}_2^-$ . Moreover, the expression for the rate constant, eq 33, indicates a second-order dependence with respect to chloride, which is not in agreement with our experimental eq 25. However, the scatter of the data in Figure 3 is so large that even a nonlinear dependence on  $[\text{Cl}^-]$  might describe the experiments.

The previous study of the  $\text{AuCl}_4^-$ -iodide reaction by Hall and Satchell<sup>8</sup> indicated a second-order dependence on chloride concentration. Their experiments were performed with use of second-order conditions with equal initial concentrations,  $[\text{AuCl}_4^-]_0 = [\text{I}^-]_0 = 1 \times 10^{-4} \text{ M}$ , and we can conclude from our present results that half of the amount of gold(III) should be rapidly reduced to gold(I) according to eq 1 under the experimental conditions used by these authors. Thus, the process observed by Hall and Satchell<sup>8</sup> was probably the slow reduction according to stoichiometric relation 12. We have tried to plot their data according to both eq 25 and eq 33 and find that the agreement with eq 33 is satisfactory. This lends some support to the mechanism, eq 29 and 30, although it should be remembered that the evaluation of rate constants in ref 8 was made by assuming second-order kinetics, which is an oversimplification.

On the other hand, the mechanism according to eq 27 and 28 is not in agreement with Hall and Satchell's data.<sup>8</sup> Even though this mechanism gives a second-order rate law for the conditions used by these authors, it will only give a first-order dependence on the chloride concentration.

It should finally be concluded that a two-electron transfer according to eq 10 coupled to an iodide release according to the reverse of eq 4 is a very unlikely mechanism for the slow reaction (vide supra). This is because reaction 4 is too slow on the time scale of the first reaction but still not a rate-determining step for the subsequent slow reaction.

The most likely mechanism for the slow reaction according to the present data is therefore given by eq 29 and 30, which are analogous to one of the mechanisms for the fast process, eq 7 and 8. Both involve a stepwise outer-sphere complex formation between tetrachloroaurate(III) and two halides, accompanied by a two-step reduction of gold(III) to gold(I) via a gold(II) intermediate. That the rate-determining step changes (cf. eq 7, 8 and 29, 30, respectively) can be accounted for by the difference in electron affinity between chloride and iodide.

**Acknowledgment.** We thank Mrs. Bodil Jönsson and Fil. mag. Ingegerd Lind for experimental assistance, the Swedish Natural Science Research Council and the Royal Physiographic Society of Lund for financial support, and one of the referees for a valuable comment on gold(II) intermediates.

**Registry No.**  $\text{AuCl}_4^-$ , 14337-12-3;  $\text{AuBr}_4^-$ , 14337-14-5;  $\text{I}^-$ , 20461-54-5.