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The Oxidation of Thiosulfate by the Tetramminegold(III) Ion in Aqueous Solution

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The stoicheiometry of the oxidation of $S_2O_3^{2-}$ by $Au(NH_3)_4^{3+}$ in acid solution is

$$Au(NH_3)_4^{3+} + 4S_2O_3^{2-} + 4H^+ \rightarrow Au(S_2O_3)_2^{3-} + S_4O_6^{2-} + 4NH_4^+$$

Reaction kinetic and equilibrium studies of the above system are interpreted in terms of the following consecutive reactions:

$$Au(NH_3)_4^{3+} + S_2O_3^{2-} \xrightarrow[H^+]{k_s} Au(NH_3)_3S_2O_3^+ + NH_4^+$$

$$Au(NH_3)_3S_2O_3^+ + 2S_2O_3^{2-} \xrightarrow[H^+,H_2O]{\text{fast}} Au(S_2O_3)_3H_2O^{3-} + 3NH_4^+$$

$$Au(S_2O_3)_3H_2O^{3-} + S_2O_3^{2-} \xrightarrow{k_r} Au(S_2O_3)_2^{3-} + S_4O_6^{2-} + H_2O$$

$k_s = 195$ $M^{-1}s^{-1}$, $\Delta H^{\ddagger} = 11.4$ kcal/mol at 25.0 °C and an ionic strength 1.0 M ($NaNO_3$).
$k_r = 1.5 \times 10^{-2}$ $M^{-1}s^{-1}$, $\Delta H^{\ddagger} = 8.4$ kcal/mol at 25.0 °C in 0.333 M $Na_2S_2O_3$.

Changes in the rate of the reduction reaction in weakly alkaline solutions accord with the reactant being the weak acid $Au(S_2O_3)_3H_2O^{3-}$ with $pK_a = 9.96$ at 25.0 °C at an ionic strength of 1.0 M. This same reactant is produced by addition of $S_2O_3^{2-}$ to solutions prepared by dissolving $NaAuCl_4.2H_2O$ in water.

Complexes of Au(III) have been much less studied than have those of Pt(II)/which is the classic example of a square planar tetracoordinated d^8 configuration metal ion, because they are more labile and also because they are more strongly oxidising. The composition of solutions prepared from Au(III) complexes is often unknown – a consequence of the increased proton acidity of the hydrolysis products. We have chosen the $Au(NH_3)_4^{3+}$ cation as reactant because it was possible, using the recent work of Skibsted and Bjerrum,[1] to choose conditions where hydrolysis was negligible.

We found that the rate of substitution of NH_3 in $Au(NH_3)_4^{3+}$ by $S_2O_3^{2-}$ was amenable to study by stopped flow spectrophotometry and was much faster than the rate of oxidation of $S_2O_3^{2-}$ by the intermediate product, a thiosulfato Au(III) complex. It then became possible to deduce the composition of this intermediate, and thus the stoicheiometry of the consecutive reaction steps from the pH changes during the reactions together with the pH dependence of the reduction rate in a series of buffers. The reduction reactions are slow enough for measurement by conventional spectrophotometry.

The general rate law for substitution in complexes of Au(III) is also that well established for those of Pt(II),

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{substituent}] \qquad (1)$$

where the first term represents solvent attack on the complex, the second term represents direct attack by the substituent, and the k_1 term is usually of much less importance for Au(III) than it is for Pt(II) complexes. The detailed mechanism of such reactions is generally accepted.[2,3] The subsequent reductions or "reductive elimination"[3] reactions,

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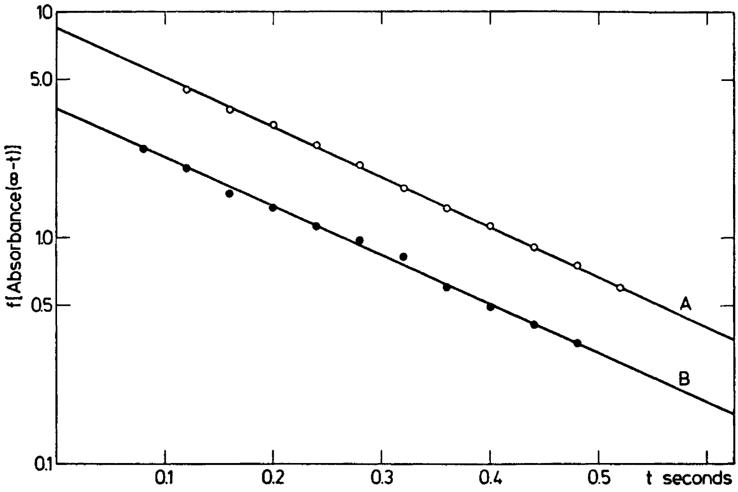


Fig. 1. Pseudo first order plots for the reaction

$$Au(NH_3)_4{}^{3+} + S_2O_3{}^{2-} \xrightarrow[H^+]{k_s} Au(NH_3)_3S_2O_3{}^{+} + NH_4{}^{+}$$

Plot of data read from stopped flow traces.
$\lambda = 480$ nm, $t = 25.0$ °C, ionic strength 1.0 M with $NaNO_3$.
A: $C_{Au(NH_3)}{}^{3+}{}_4 = 1.13$ mM, $C_{S_2O_3}{}^{2-} = 0.025$ M, $C_{H^+} = 5.6$ mM.
B: $C_{Au(NH_3)_3}{}^{3+} = 0.55$ mM, $C_{S_2O_3}{}^{2-} = 0.025$ M, $C_{H^+} = 5.0$ mM.

analogous to that which occurs in the present system, have however been very little studied. In the present work we combine our results with those from one earlier investigation[4] which we find pertinent, and attempt to evaluate the usefulness of two alternative mechanisms as tools for predicting further definitive experiments.

EXPERIMENTAL

$[Au(NH_3)_4](NO_3)_3$ was prepared as in Ref. 1. All other chemicals were analytical grade. Water was doubly distilled in an all quartz apparatus. $Na_2S_2O_3$ solutions were used immediately after preparation.

The stopped flow apparatus was that described in Ref. 5 and the other measurements were made with a thermostatted Cary 14 recording spectrophotometer and with a digital pH meter (PH M 52 Radiometer) fitted with a glass electrode (Radiometer Type G202C).

All pH measurements and calculations were based on concentration standards in the actual media.

RESULTS

Substitution reaction. The rate of formation of the yellow-brown colour which appeared on mixing solutions of $[Au(NH_3)_4](NO_3)_3$ and of $Na_2S_2O_3$ was measured at 410 nm and at 480 nm by the stopped flow technique. The reaction was investigated in weakly acid

Table 1. Rate constant for the reaction[a]

$$Au(NH_3)_4{}^{3+} + S_2O_3{}^{2-} \xrightarrow[H^+]{k_s} Au(NH_3)_3S_2O_3{}^{+} + NH_4{}^{+}.$$

t °C	k_s $M^{-1}s^{-1}$	Number of runs
21.0	148 ± 5	3
25.0	195 ± 5	13[b]
30.0	272 ± 10	5

[a] C_{HNO_3} 5.0 to 7.0 mM. $C_{Au(NH_3)_4}{}^{3+}$ 0.55 to 1.13 mM. $C_{S_2O_3}{}^{2-}$ 0.025 to 0.050 M. Ionic strength 1.0 M, adjusted with $NaNO_3$. [b] Two pseudo first order plots are given in Fig. 1.

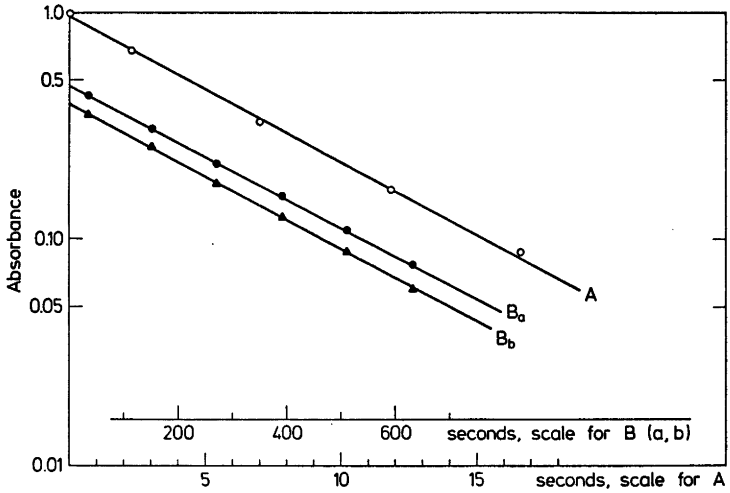


Fig. 2. Pseudo first order plots for the formation of $Au(S_2O_3)_2^{3-}$.
A: $C_{Au(NH_3)_4^{3+}} = 3.43$ mM, $C_{S_2O_3^{2-}} = 0.25$ M, pH = 10.75, $\lambda = 410$ nm, $t = 25.0$ °C, ionic strength 1.0 M with $NaNO_3$. Zero time in the plot corresponds to about five seconds after mixing.
B: $C_{Au(NH_3)_4^{3+}} = 8.57$ mM, $C_{S_2O_3^{2-}} = 0.10$ M, pH = 4.8, $t = 25.0$ °C, ionic strength 1.0 M with $NaNO_3$. B_a: $\lambda = 410$ nm, B_b: $\lambda = 390$ nm.

Table 2. pH dependence of rate of formation of $Au(S_2O_3)_2^{3-}$. Ionic strength 1.0 M (Na_2SO_4), 25.0 °C.[a]

$C_{Au(NH_3)_4^{3+}}$ M	$C_{S_2O_3^{2-}}$ M	pH	$k_{obs} \times 10^3$ s^{-1}	pK_a
0.00111	0.200	3.90	2.96	
0.00111	0.200	4.53	3.06	
0.00111	0.200	4.86	3.00	
0.00111	0.200	5.52	2.96	
0.00111	0.200	6.97	3.20	(9.82)
0.00111	0.200	7.29	3.49	(9.78)
0.00111	0.200	8.30	6.62	9.94
0.00111	0.200	8.80	13.9	9.90
0.00111	0.200	8.88	15.4	9.91
0.00111	0.200	9.03	18.5	9.96
0.00111	0.200	9.10	20.1	9.98
0.00111	0.200	9.12	21.3	9.97
0.00444 [b]	0.167	9.88	71.2	9.94
0.00343 [b]	0.100	10.66	128	
0.00343 [b]	0.150	10.71	157	
0.00343 [b]	0.200	10.75	150	
0.00343 [b]	0.250	10.75	144	

[a] $pK_a = pH + \log(\alpha/(1-\alpha))$,

$$\alpha = \frac{[Au(S_2O_3)_3H_2O^{3-}]}{[Au(S_2O_3)_3H_2O^{3-}] + [Au(S_2O_3)_3OH^{4-}]} = (k_{obs} - k_b)/(k_a - k_b).$$

$10^3 k_b = 150$ s^{-1}; $10^3 k_a = 15[S_2O_3^{2-}]$ s^{-1}. [b] In 1.0 M $NaNO_3$.

Table 3. Rate laws used in interpretation of the rate of the reductive elimination reaction, *cf.* Scheme 1.[a]

$$-\mathrm{d}([\mathrm{Au(S_2O_3)_3H_2O^{3-}}]+[\mathrm{Au(S_2O_3)_3OH^{4-}}])/dt=k_{\mathrm{obs}}[\mathrm{Au(S_2O_3)_3H_2O^{3-}}]$$

pH range studied	Rate law
3.9 – 6.5	$k_{\mathrm{obs}}=k_{\mathrm{a}}^{\mathrm{o}}+k_{\mathrm{a}}[\mathrm{S_2O_3^{2-}}]$
7.0 – 9.9	$k_{\mathrm{obs}}=\alpha k_{\mathrm{a}}^{\mathrm{o}}+\alpha k_{\mathrm{a}}[\mathrm{S_2O_3^{2-}}]+(1-\alpha)k_{\mathrm{b}}$ $\alpha/(1-\alpha)=[\mathrm{H^+}]/K_{\mathrm{a}}$ $\mathrm{p}K_{\mathrm{a}}=9.96\pm0.01$
10.6 – 10.8	$k_{\mathrm{obs}}\approx k_{\mathrm{b}}$

[a] Experimental values at 25.0 °C in 1.0 M medium:

$k_{\mathrm{a}}^{\mathrm{o}}=2\times10^{-4}\ \mathrm{s^{-1}}$ (corrected to 2nd order: $4\times10^{-6}\ \mathrm{M^{-1}\ s^{-1}}$.)
$k_{\mathrm{a}}=1.5\times10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$
$k_{\mathrm{b}}=0.15\ \mathrm{s^{-1}}$ (corrected to 2nd order: $2.7\times10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$.)

Table 4. $C_{\mathrm{S_2O_3}^{2-}}$ dependence of rate of formation of $\mathrm{Au(S_2O_3)_2^{3-}}$ at constant pH near 9.0. Ionic strength 1.0 M with $\mathrm{Na_2SO_4}$. 25.0 °C. $C_{\mathrm{Au(NH_3)_4}^{3+}}=1.11$ mM.[a]

$C_{\mathrm{S_2O_3}^{2-}}$ M	pH	$10^3\,k_{\mathrm{obs}}\ \mathrm{s^{-1}}$	$10^3\,k_{\mathrm{calc}}\ \mathrm{s^{-1}}$
0.333	8.95	20.4	20.0
0.250	8.97	18.8	18.8
0.167	8.99	18.7	18.7
0.0833	9.01	17.6	17.7
0.0333	9.01	16.2	16.2

[a] $k_{\mathrm{calc}}=\alpha(k_{\mathrm{a}}^{\mathrm{o}}+k_{\mathrm{a}}[\mathrm{S_2O_3^{2-}}])+(1-\alpha)k_{\mathrm{b}}$; $k_{\mathrm{a}}^{\mathrm{o}}=2\times10^{-4}\ \mathrm{s^{-1}}$; $k_{\mathrm{a}}=1.5\times10^{-2}\ \mathrm{M^{-1}s^{-1}}$; $k_{\mathrm{b}}=0.15\ \mathrm{s^{-1}}$.

solution to ensure that the tetrammine and not an amido complex was the reactant. At thiosulfate/gold(III) ratios lower than 4 the product solutions gave a precipitate and were not investigated further. At ratios ≫ 4, pseudo first order plots were linear throughout with no interference from the subsequent reduction (see Fig. 1).

The reaction was first order in each of the reactants and no solvent path corresponding to the k_1 term of eqn. 1 could be detected. We assume that reaction (2) is rate determining. This assumption is based on the known substitution behaviour of all similar complexes and is also the simplest way of interpreting the data.

$$\mathrm{Au(NH_3)_4^{3+}+S_2O_3^{2-}}\ \underset{\mathrm{H^+}}{\xrightarrow{k_s}}\ \mathrm{Au(NH_3)_3S_2O_3^{+}+NH_4^{+}} \quad (2)$$

The data for k_s in Table 1 give a good linear Arrhenius plot. From this, and using reaction rate theory, we calculate that $\Delta H^{\ddagger}=11.4$ kcal/mol and $\Delta S^{\ddagger}=-10$ cal/mol K.

pH Measurements and stoicheiometry. The experiments were performed with different concentrations of nitric acid, the final pH ranging from 3 to 9. For the acid solutions $\mathrm{p}K_{\mathrm{a}}$ of $\mathrm{HS_2O_3^-}$ was taken as 1.01 in the 1 M media.[6] The pH of solutions of the substitution product was always found to be that calculated for liberation of all four ammonia molecules from the metal complex.

Reaction (2) is thus followed by

$$\mathrm{Au(NH_3)_3S_2O_3^{+}+2S_2O_3^{2-}+H_2O}\ \underset{\mathrm{H^+}}{\xrightarrow{\text{fast}}}\ \mathrm{Au(S_2O_3)_3H_2O^{3-}+3NH_4^{+}} \quad (3)$$

The visible spectrum of this intermediate product is a broad band, $\lambda_{\mathrm{max}}\approx410$ nm, $\varepsilon_{\mathrm{max}}\approx600\ \mathrm{cm^{-1}\ M^{-1}}$. The pH of all solutions remained constant during the fading of this yellow-brown colour which was used to follow the rate of the reductive elimination reaction. This confirmed negative tests for $\mathrm{SO_4^{2-}}$ and together with the presence of the colourless thermodynamically very stable[7] $\mathrm{Au(S_2O_3)_2^{3-}}$ as a product gave the overall stoichiometry as

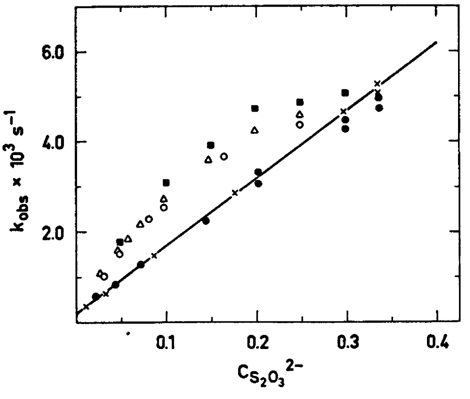


Fig. 3. Pseudo first order rate constants for the reductive elimination reaction

$$Au(S_2O_3)_3H_2O^{3-} + S_2O_3^{2-} \xrightarrow{k_{obs}} Au(S_2O_3)_2^{3-} + S_4O_6^{2-} + H_2O$$

at pH = 6.3 and 25.0 °C as a function of $C_{S_2O_3^{2-}}$. The reactant $Au(S_2O_3)_3H_2O^{3-}$ is produced from $Au(NH_3)_4^{3+}$ (●, ○, ■) or from $AuCl_n(OH)_m(H_2O)_{4-n-m}^{(3-n-m)+}$ (×, △). Ionic strength is in all experiments 1.0 M, adjusted with Na_2SO_4 (×, ●), $NaNO_3$ (*Δ*, ○) or with $NaClO_4$ (■). The straight line represents the experiments in the $Na_2(SO_4,S_2O_3)$ medium where C_{Na^+} as well as ionic strength are constant. All experiments with $C_{S_2O_3^{2-}} = 0.333$ M correspond to a pure $Na_2S_2O_3$ medium.

$$Au(NH_3)_4^{3+} + 4\ S_2O_3^{2-} \xrightarrow[H^+]{} Au(S_2O_3)_2^{3-} + 4\ NH_4^+ + S_4O_6^{2-}$$

Reductive elimination reaction. The rate of this reaction and the order in thiosulfate was found to be pH dependent, but was in all cases first order in complex. The kinetic experiments were performed with excess of thiosulfate giving experimental first or pseudo first order conditions (see Fig. 2). The reaction was followed at each 10 nm in the wavelength range 370 to 450 nm and no wavelength dependence on rate was found. The compositions of some of the solutions together with the pseudo first order rate constants are given in Tables 2 and 4. The pH of the solutions was adjusted either with nitric acid or with small concentrations of ammonium nitrate and ammonia, potassium hydrogen phthalate, sodium hydrogen orthophosphate, borax, or sodium acetate and acetic acid, buffers. The pH of the reaction mixture was measured in all experiments. The buffer component did not affect the rates.

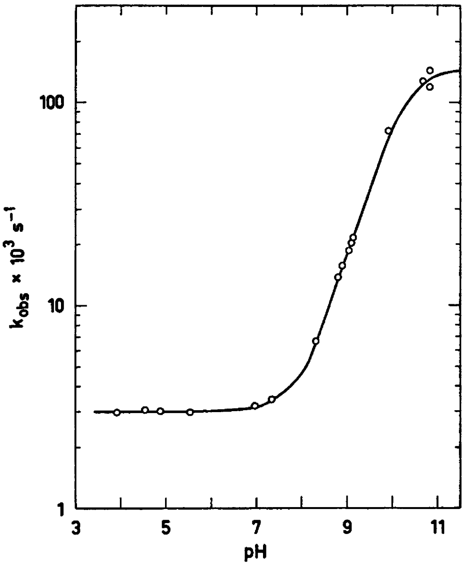


Fig. 4. pH dependence of rate of formation of $Au(S_2O_3)_2^{3-}$ at ionic strength 1.0 M and 25.0 °C. Experimental points from Table 2. Calculated line from rate laws given in Table 3.

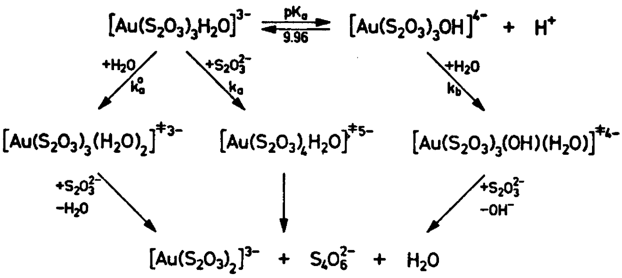
The rate of reduction is independent of hydrogen ion concentration in the pH range 3 to 6.5. Below pH ∼ 3 the decomposition of thiosulfate excludes further investigation. Fig. 3 gives the pseudo first order constants at 25.0 °C and ionic strength 1.0 M with pH adjusted to 6.3 as a function of thiosulfate concentration. Salt effects are large, but in a

Table 5. Temperature dependence of the reductive elimination reaction

$$Au(S_2O_3)_3H_2O^{3-} + S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + S_4O_6^{2-} + H_2O$$

Experiments under pseudo first order conditions in 0.333 M $Na_2S_2O_3$ at pH = 6.3. $C_{Au(NH_3)_4^{3+}} = 1.20$ mM.

t °C	k_{obs} s^{-1} × 10^3
19.5	3.37
21.7	3.76
24.2	4.44
26.2	4.92
28.0	5.42
31.1	6.30
34.4	7.02



Scheme 1.

sodium sulfate thiosulfate medium where the ionic strength as well as the sodium ion concentration are constant the reactions are first order in both complex and (excess) thiosulfate. Fig. 3 also illustrates that the same behaviour is found with solutions prepared from $NaAuCl_4$ and thiosulfate. It should be noted that as the $AuCl_4^-$ is hydrolysed in water, the aquo thiosulfato gold(III) reactant is, in these solutions, produced by substitution of $S_2O_3^{2-}$ in $AuCl_n(OH)_m(H_2O)_{4-n-m}^{(3-n-m)+}$ complexes.*

Fig. 4 is a semilogarithmic plot of the pH profile for the observed rate of reduction at constant thiosulfate concentration. At the highest pH studied (10.60 – 10.75) there is a limiting rate, within experimental error independent of thiosulfate concentration. The pH dependence and the dependence on thiosulfate concentration on the observed rate fit the rate law given in Table 3. Table 4 illustrates the accuracy with which the thiosulfate dependence at intermediate and constant pH can be reproduced. The activation parameters for the k_a path (see Tables 3 and 5 and Scheme 1) in 0.333 M $Na_2S_2O_3$ are: $\Delta H^{\ddagger} = 8.4$ kcal/mol, $\Delta S^{\ddagger} = -46$ cal/mol K. In calculating these we did not correct for the effect of the small, poorly defined, intercept in Fig. 3.

DISCUSSION

The rate of substitution of NH_3 in $Au(NH_3)_4^{3+}$ by $S_2O_3^{2-}$ is much faster than is the solvent substitution. This is in accordance with the well known increased nucleophilic character of the substitution. The bimolecular substitution can be supposed to take place through a five coordinate trigonal bipyramidal reactive complex as suggested for other d^8 systems. The rate and activation parameters for this reaction thus supplement the rather sparse earlier data for cationic Au(III) complexes.

The mechanism of the reductive elimination reaction is more speculative in that, firstly, measurements could only be made in an excess of $S_2O_3^{2-}$ so that the composition of the reactant complex could not be directly determined and secondly, it cannot be assumed that the reaction path for reductive elimination is analogous to that for substitution.

We believe that the reactant is $Au(S_2O_3)_3H_2O^{3-}$ on the following grounds.

From the lack of pH change during reduction

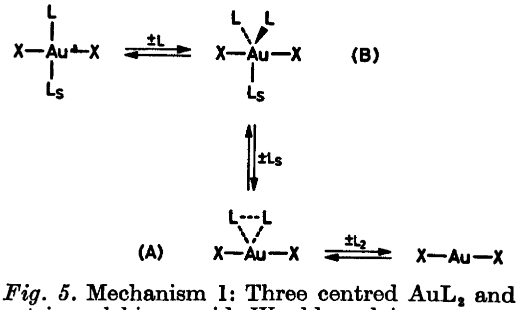


Fig. 5. Mechanism 1: Three centred AuL_2 and a trigonal bipyramid. Would explain:

1. The gold(III) – thiosulfate reaction. $L_s = H_2O$, $X = L = S_2O_3^{2-}$.
2. The iodide catalysed formation of *trans*-$Au(CN)_2I_2^-$. $X = CN^-$, $L = L_s = I^-$.

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*Preliminary experiments with $NaAuCl_4$ in weakly acid 1 M NaCl and with $KAuBr_4$ in weakly acid 1 M NaBr, where the gold(III) is almost exclusively present as the tetrahalogenidoaurate(III) ion, showed that reduction is rapid and that no intermediate yellowbrown thiosulfato gold(III) complex was detectable.

In completely hydrolysed gold(III) solutions where $Au(OH)_4^-$ and polymers dominate, we find that the rate of substitution of the first thiosulfate is of the same order of magnitude as the reductive elimination.

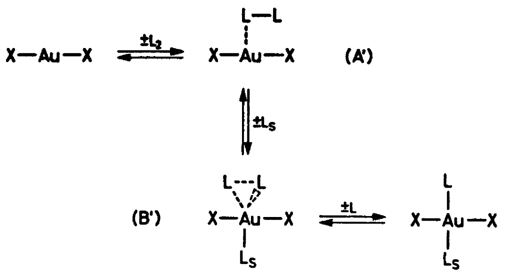

Fig. 6. Mechanism 2: Oxidation is attack on electron pair of Au(I) by L_2; back reaction is attack by L^- on L coordinated to Au(III). Would explain *trans* product and solvent dependence of $Au(CN)_2I_2^-$ formation and, for $L_S = I^-$, also the I^- catalysed path. For the thiosulfate reduction this means rate determining attack by $S_2O_3^{2-}$ on coordinated $S_2O_3^{2-}$.

and the initial pH changes before reduction then no NH_3 is present. This is confirmed by the fact that the same species is produced from chlorohydroxo Au(III) complexes.

Changes in the rate of reduction with pH show that the reactant is a weak acid, $pK_a = 9.96$. We think that the alternative formulation as $Au(S_2O_3)_4H^{4-}$ is (in view of the strength [6] of uncomplexed $HS_2O_3^-$) very unlikely and that, therefore, the acid ligand is a water molecule. The reduction rate in acid solution is first order in $[S_2O_3^{2-}]$ and the overall stoicheiometry $4S_2O_3^{2-} + 1Au(III)$. From the charge repulsion of the reactants successive additions of $S_2O_3^{2-}$ should proceed with progressively slower rates unless other factors are involved.

The following extra experimental facts are in accord with this interpretation, but are not definitive. Thus, the kinetic ionic strength effect is large and positive but the media used are outside the theoretically predictable range. Similarly, the large negative $\Delta S^{\ddagger}$ and the large kinetic specific Na^+ effect also would be expected but cannot be used quantitatively.

Our interpretation of the reaction paths necessary to explain the complete reduction rates is given in Scheme 1.

Experimental data such as that reported here, and for one system alone, cannot profitably be used to deduce the detailed mechanism of the reductive elimination. We find, however, that one other Au(III) – Au(I) system has been subjected to detailed study and discuss this below, together with our results, chiefly in order to attempt to define the problems needing to be solved and to suggest experiments which may aid in the solution of these problems.

Ford-Smith *et al.*[4] studied the oxidative-*addition* reaction $Au(CN)_2^- + I_2 \rightarrow$ *trans*-$Au(CN)_2I_2^-$ and found the following two term rate law:

$$d[Au(CN)_2I_2^-]/dt = k_2[Au(CN)_2^-][I_2] + k_3[Au(CN)_2^-][I_2][I^-]$$

They also found that the rate of reduction of $Au(CN)_2I_2^-$ is dependent on [X] where X is an organic substance known to react with I_2. We suggest that either of the following two mechanisms depicted in Figs. 5 and 6 which incorporate ideas of earlier workers [2,3] for similar reactions of metal complexes but involving a $d^6 - d^8$ electronic configuration change, could explain the above limited data presently available for $d^8 - d^{10}$ complexes.

In Fig. 5 (Mechanism I) the formation of a three centred AuL_2 and a trigonal bipyramid would explain

1. the $Au(III) - S_2O_3^{2-}$ reaction, $L_S = H_2O$, $X = L = S_2O_3^{2-}$;
2. the I^- catalysed formation of *trans*-$Au(CN)_2I_2^-$, $X = CN^-$, $L = I^-$.

In Fig. 6 (Mechanism II) oxidation occurs by attack on an electron pair of Au(I) by L_2 while the back reaction is attack by L^- on L coordinated to Au(III). This would explain *trans*-product and solvent dependence of $Au(CN)_2I_2^-$ formation, and, for $L_S = I^-$, also the I^- catalysed path. For the thiosulfate reduction this means rate determining attack by $S_2O_3^{2-}$ on the S atom of the coordinated $S_2O_3^{2-}$. Whether such direct attack on the coordinated S of the ligand does occur may possibly be tested experimentally by examining the magnitude of the changes in activation enthalpy with changes of the coordinated axial ligands. The present work does show, however, that when these axial ligands are Cl^- or NH_3 then no reduction occurs. Direct attack on coordinated S would thus be less than the substitution rate. The trigonal bipyramidal intermediate of the substitution reaction is included in both mechanisms. The linear

X – Au – X group remains effectively unchanged during the reactions. It would seem probable that the extent to which the transition state for the rate determining step resembles the extreme forms B and A′ (in Figs. 5 and 6) depends on the degree of metal bonding to the extra ligand depicted in Figs. 5 and 6 as L_s.

We have confined the above discussion to the two reactions giving the rate constants (k_s and k_a in tables) which we have studied in detail and over a range of temperature. The reduction reaction of the conjugate base will be the subject of a further study.

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