Reduction of Gold(III) to Gold(I) by Dialkyl Sulphides. Evidence for an Atom-transfer Redox Process

By **Giuliano Annibale, Luciano Canovese, Lucio Cattalini,** and **Giovanni Natile,*** Istituto di Chimica Generale ed Inorganica, Università di Venezia, Italy

A kinetic study of the reduction of gold(III) to gold(I) by dialkyl sulphides, in aqueous methanol, is reported. The reaction takes place in two steps. In the first step, substitution equilibria which are strongly dependent on the bulkiness of the entering sulphide are set up. In the second step, the gold(III) complexes react with an extra molecule of sulphide to give gold(I) species and sulphoxide; very likely the reductant attacks the substrate at a chlorine and not at the metal centre, the halogen is then transferred from gold to sulphur leaving an electron pair on the metal. The reactivity of the gold(III) substrates increases with increasing substitution $\{[AuCl_4]^- \ll [AuCl_3(SR_2)] < [AuCl_2(SR_2)_2]^+\}$ paralleling the increasing positive charge on the complex; on the other hand that of the sulphides parallels their basicity ($SMe_2 < SEt_2 < SPr^i_2$) indicating that in the redox step polar effects are more important than steric ones. The reaction rate also exhibits a marked solvent dependence, and increases with increasing percentage of water in the reaction medium, the relationship of log $k_{1,2}$ to solvent polarity being linear.

THE majority of kinetic studies of gold(III) complexes deal with nucleophilic substitution [1] and very few with reactions which involve redox processes.[2-6] In the kinetic studies of the latter type different mechanisms have been proposed: (*i*) nucleophilic attack of the reductant, L, on the hydroxyl ion of a hydrolysed gold(III) species; [2] (*ii*) attachment of L to an axial co-ordination site of the gold(III) complex with formation of an intermediate of higher co-ordination number which undergoes rapid intramolecular electron transfer; [3] and finally (*iii*) ligand substitution by L followed by rapid internal electron transfer.[4,5]

The absence of analogies between these mechanisms and those found in complementary redox reactions involving platinum(IV) complexes,[1] which usually take place through an atom-transfer process, prompted us to investigate further the redox reaction in the gold(III) case. In fact, although the gold(III) complexes are four-co-ordinate while the platinum(IV) species are six-co-ordinate (and this could be a good reason for a different mechanism), in both cases the redox process lowers by two units both the co-ordination number and the oxidation number of the metal.

Moreover, a clear understanding of the reduction mechanism of gold(III) chloride by dialkyl sulphides would be very useful for the elucidation of the mechanism of stereospecific oxidation of methionine to methionine sulphoxide promoted by tetrachloroauric acid, which has been reported by some of us.[7]

EXPERIMENTAL

Hydrogen tetrachloroaurate(III) trihydrate was obtained from Johnson, Matthey and Co.; solvents, inorganic acids and salts, dimethyl, diethyl, and di-isopropyl sulphide were all reagent grade products.

Preparations.—The $[AuCl_3(SR_2)]$ complexes ($SR_2 = SMe_2$, SEt_2, or SPr^i_2) were prepared by the method of Ray and Sen.[8] Bromodimethylsulphonium bromide $[SMe_2Br]Br$ and methoxydimethylsulphonium perchlorate $[SMe_2(OMe)][ClO_4]$ were prepared by reported procedures.[9,10]

Kinetics.—Rate data were obtained spectrophotometrically by measuring changes of absorbance with time using Perkin-Elmer 175 and 575 spectrophotometers. The changing absorbance of the reacting solution was measured at 310 nm by scanning at constant wavelength.

Separate solutions of complex and reagents were prepared in methanol containing the appropriate percentage of water, brought to reaction temperature, and mixed in the thermostatted cell of the spectrophotometer. Either $[AuCl_4]^-$ or $[AuCl_3(SR_2)]$ was used as starting substrate, in the latter case the complex solution was prepared just before use.

All the kinetic runs were performed under pseudo-first-order conditions, and at constant ionic strength.

First-order rate constants were calculated from plots of $\ln(A_t - A_\infty)$ against time, where A_t and A_∞ are absorbances at time t and after at least six half-lives respectively. These plots were linear for at least four half-lives. The experimentally determined rate constants, $k_{obs.}/s^{-1}$, are reported in Tables 1—3. The values of equilibrium and kinetic constants (except K_1 which was determined directly from spectrophotometric measurements) were calculated by best-fitting procedures and are reported in Tables 4 and 5; the quoted uncertainties are 95% confidence limits.

TABLE 1

Values of $k_{obs.}$ for the reduction of gold(III) chloride by dimethyl sulphide in methanol containing 5% water at $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$) and 25 °C

$10^3[SMe_2]$/mol dm^{-3}	$10^3[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}/s^{-1}$
5.38	7.46	3.37
5.38	11.2	2.88
5.38	18.7	2.38
8.08	3.73	8.77
8.08	7.46	6.16
10.8	3.73	14.0
10.8	3.73	13.5
10.8	7.46	9.75
10.8	7.46	9.03
13.5	3.73	18.4
13.5	3.73	18.8
13.5	7.46	12.4
13.5	7.46	12.7
16.2	3.73	25.1
16.2	7.46	16.8
17.8	2.47	38.8
18.8	1.31	51.4
18.8	1.83	48.8
18.8	2.62	40.3
18.8	3.73	33.3

Equilibrium Constants.—The equilibrium constant for the substitution reaction $[AuCl_4]^- + SR_2 \rightleftharpoons [AuCl_3(SR_2)] + Cl^-$ was determined spectrophotometrically by plotting the function $(A_1 - A_x)/(A_x - A_2)$ against $[SR_2]/[Cl^-] = x$, where A_1 and A_2 are absorbances, at 310 nm, of equimolar solutions of $[AuCl_3(SR_2)]$ and $[AuCl_4]^-$ respectively and A_x the absorbance of a solution having the same total concentration of gold complexes and a value of $[SR_2]/[Cl^-] = x$. This function is equal to $[AuCl_3(SR_2)]/[AuCl_4^-]$ which, in turn, is equal to $K_1([SR_2]/[Cl^-])$ and so the resulting plot should be a straight line with slope K_1.

TABLE 2

Values of $k_{obs.}$ for the reduction of gold(III) chloride by diethyl sulphide at different values of ionic strength and percentage of water in methanol at 25 °C

$10^3[SEt_2]$/mol dm^{-3}	$10^3[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
(*a*) $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$), 5% water		
3.56	5.87	6.85
7.13	1.17	13.3
7.13	1.76	42.6
7.13	1.76	44.5
7.13	2.35	34.4
7.13	2.93	30.9
7.13	3.52	26.8
7.13	5.86	19.5
7.13	17.6	10.8
7.13	23.5	9.60
7.13	35.1	7.94
7.13	46.9	6.55
10.7	17.6	20.2
14.2	23.4	25.3
17.8	29.3	32.6
21.4	35.2	39.0
(*b*) $I = 0.106$ mol dm^{-3} ($Li[ClO_4]$), 5% water		
7.12	3.23	45.0
7.12	3.23	45.7
7.12	4.71	31.7
7.12	5.86	27.5
7.12	7.06	25.3
7.12	7.06	26.4
7.12	9.41	21.2
7.12	11.7	19.0
7.12	17.6	15.2
7.12	23.5	13.2
7.12	29.3	11.7
7.12	35.2	10.7
7.12	46.8	9.98
7.12	58.8	8.73
7.12	58.8	8.38
7.12	70.5	7.88
7.12	81.8	7.48
7.12	93.6	6.65
7.12	106	6.87
(*c*) $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$), 2% water		
7.20	1.75	24.8
7.20	2.34	19.7
7.20	3.51	14.2
7.20	4.68	13.0
7.20	5.85	11.0
7.20	11.7	8.08
7.20	23.5	6.27
7.20	35.1	5.39
7.20	46.8	4.91
(*d*) $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$), 10% water		
3.15	1.77	28.9
3.15	2.36	24.6
3.15	2.95	20.8
3.15	4.72	15.9
3.15	5.89	14.0
3.15	11.8	10.2
3.15	17.7	8.15
3.15	29.4	6.80
3.15	47.0	5.89

In order to calculate $(A_1 - A_x)/(A_x - A_2)$ it is sufficient to know a couple of values, A_x and A_2, corresponding to the same total gold concentration, and the parameter A_1/A_2 which is constant.

Pairs of values, A_x and A_2, were obtained in the following way. A microquantity of $[AuCl_3(SR_2)]$ was placed in the thermostatted cell of the spectrophotometer containing an appropriate volume of a solution of known x. Since in these conditions the redox reaction also occurs, the change of absorbance with time was monitored for 2—3 min. Then, using a micropipette, a known volume (about $\frac{1}{10}$ that of the cell) of a very concentrated (at least 100 times that of the previous solution) LiCl solution was added to the cell, and the change of absorbance monitored for a few minutes. The exact values of A_x and A_2 were then calculated by extrapolating to zero mixing time, the former and the latter curve of changing absorbance (these were nearly straight lines), and making a correction for dilution on the measured value of A_2.

TABLE 3

Values of $k_{obs.}$ for the reduction of gold(III) chloride by di-isopropyl sulphide in methanol containing 5% water at $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$) and 25 °C

$10^3[SPr^i_2]$/mol dm^3	$10^3[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
4.18	44.5	2.56
4.60	10.9	8.04
4.60	43.5	3.49
5.91	9.31	11.6
5.91	41.9	5.30
6.45	2.57	20.4
7.31	5.75	18.7
7.53	4.45	21.2
8.28	2.44	26.8
8.28	9.78	17.6
8.28	37.6	9.37
8.28	39.1	8.91
8.81	1.93	30.5
10.4	36.7	13.2
11.8	34.9	16.0

The value of A_1/A_2 was calculated from pairs of values, A_1 and A_2 (corresponding to the same gold concentration) obtained, as above, by dissolving a microquantity of $[AuCl_3(SR_2)]$ in a solution containing no chloride, and then adding a large excess of LiCl.

TABLE 4

Values of equilibrium and kinetic constants of equation (2) relative to SMe_2, SEt_2, and SPr^i_2, obtained from data in methanol containing 5% water at $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$) and 25 °C

	$\frac{k_1}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	K_1	$\frac{k_2K_2}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$
SMe_2*	0.41 ± 0.10	27.0 ± 5.0	
SEt_2	1.24 ± 0.12	18.7 ± 2.8	1.23 ± 0.06
SPr^i_2	2.94 ± 0.30	2.85 ± 0.25	0.19 ± 0.12

* $k_2 = 5.03 \pm 0.90$ dm^3 mol^{-1} s^{-1}, $K_2 = 0.08 \pm 0.02$.

N.m.r. spectra were recorded on a Varian EM 390 spectrometer. All solutions were prepared in AnalaR [$^2H_4$]-methanol (99.5%), and care was taken to ensure that the materials were dried as much as possible and stored and handled in dry conditions.

TABLE 5

Values of equilibrium and kinetic constants of equation (2) relative to SEt_2 obtained from data at different values of ionic strength and percentage of water in methanol, and at 25 °C

Water %	I mol dm^{-3}	k_1 dm^3 mol^{-1} s^{-1}	K_1	k_2K_2 dm^3 mol^{-1} s^{-1}
2	0.047	0.81 ± 0.08	19.8 ± 2.2	0.64 ± 0.04
5	0.047	1.24 ± 0.12	18.7 ± 2.8	1.23 ± 0.06
5	0.106	1.42 ± 0.10	20.2 ± 1.7	2.27 ± 0.10
10	0.047	3.00 ± 0.48	17.4 ± 2.8	3.71 ± 0.40

RESULTS

A two-step reaction is observed when $[AuCl_4]^-$ and SR_2, in excess, are allowed to react in methanol. The first step is accompanied by a considerable increase in absorbance and corresponds to the formation of substitution products in equilibrium with the starting $[AuCl_4]^-$ ion. In the second step the absorbance falls nearly to zero and corresponds to the reduction of the gold(III) complexes to colourless gold(I) species, the latter being stable in the presence of an excess of sulphide.

The progress of the redox reaction was followed spectrophotometrically at 310 nm under pseudo-first-order conditions where $[Cl^-]$, $[SR_2] \gg$ [Complex]. The dependence of the rate constant upon $[Cl^-]$, $[SR_2]$, ionic strength, and percentage of water in the methanol solution was considered; preliminary experiments showed that addition of perchloric acid up to a concentration of 3.5×10^{-3} mol dm^{-3} did not affect the rate.

First we carried out a set of experiments at a constant value of $[SR_2]/[Cl^-]$. Under these conditions the composition of the equilibrium mixture, of $[AuCl_4]^-$ and substituted species, is kept constant thereby not contributing to changes in the reaction rate. The pseudo-first-order rate constants, so obtained, plotted against $[SR_2]$ gave a straight line passing through the origin (Figure 1); this indicates that any gold(III) species requires the participation of an extra molecule of thioether in order to undergo the redox process.

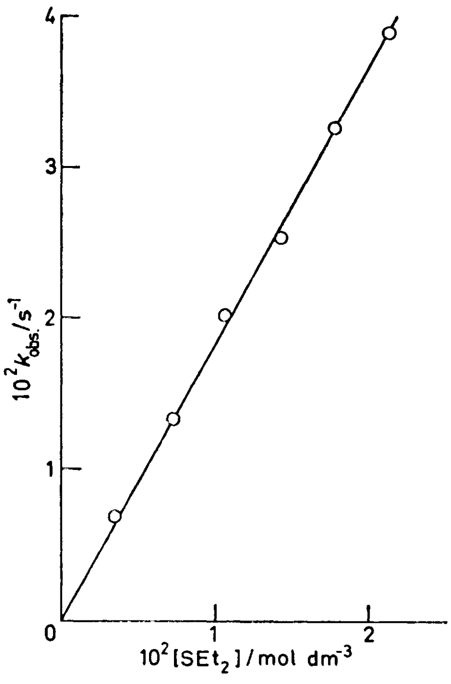


FIGURE 1 Plot of $k_{obs.}$ against $[SR_2]$ for the reduction of gold(III) chloride by SEt_2 at constant ratio $[SR_2]/[Cl^-] = 0.607$. Solvent, methanol containing 5% water; $I = 0.047$ mol dm^{-3} ($Li[ClO_4]$), 25 °C

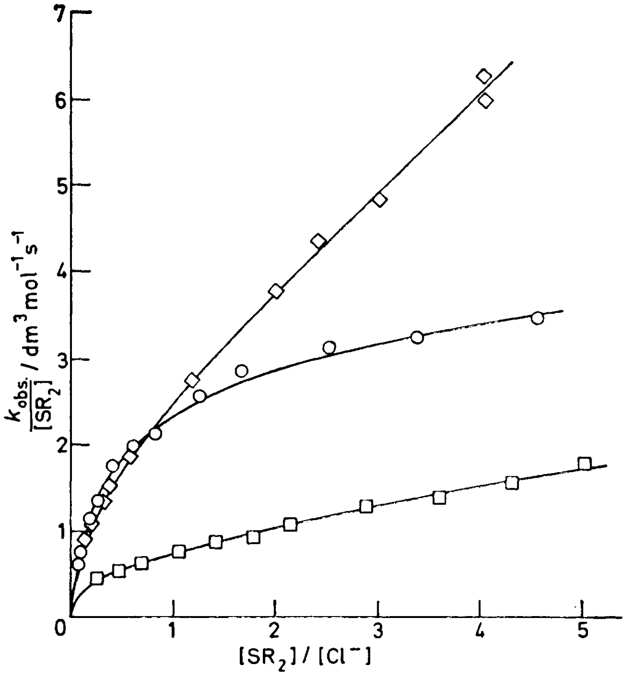


FIGURE 2 Plot of $k_{obs.}/[SR_2]$ against $[SR_2]/[Cl^-]$ for the reduction of gold(III) chloride by SMe_2 (□), SEt_2 (◇), and SPr^i_2 (○). Other conditions as in Figure 1

Information on the substitution equilibria which precede the redox step was obtained by examining the change of $k_{obs.}/[SR_2]$ (*i.e.* the slope of the above diagrams obtained at constant $[SR_2]/[Cl^-]$) as a function of $[SR_2]/[Cl^-]$.

Reaction with Dimethyl Sulphide.—The experimental data, plotted in Figure 2, fit the empirical expression (1) which is

$$k_{obs.}/[SR_2] = (rx + sx^2)/(1 + tx + ux^2) \qquad (1)$$
$$(x = [SR_2]/[Cl^-])$$

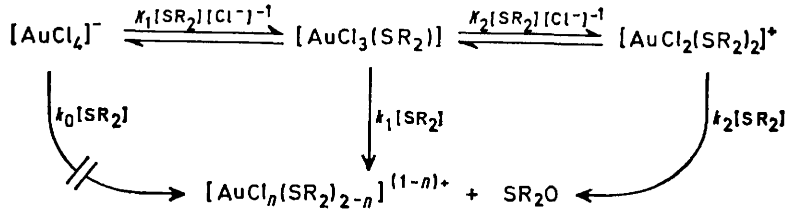
in accord with two substitution processes (leading to the formation of mono- and di-substituted species) preceding the redox step. On this basis Scheme 1 can be proposed which gives equation (2) for the rate expression.

$$k_{obs.} = \left(\frac{k_0 + k_1K_1[SR_2][Cl^-]^{-1} + k_2K_1K_2[SR_2]^2[Cl^-]^{-2}}{1 + K_1[SR_2][Cl^-]^{-1} + K_1K_2[SR_2]^2[Cl^-]^{-2}}\right)[SR_2] \qquad (2)$$

From comparison of equations (1) and (2) it follows that the contribution of k_0 to the reaction rate is negligible and therefore $[AuCl_4]^-$ is not a reactive species towards reduction. This inertness of $[AuCl_4]^-$ was also confirmed in the reaction with SEt_2 and SPr^i_2.

The values of k_1, k_2, K_1, and K_2 can be calculated from r, s, t, and u. The last parameters, however, could not be determined directly from curve-fitting procedure since more than one set of data were in accord with the experimental diagram within the limits of experimental error. On the other hand the best-fitting procedure gave reliable values of r, s, and u provided that the value of t ($t = K_1$) was given. This could be determined independently from spectrophotometric measurement of the equilibrium constant K_1 (see Experimental section).

Reaction with Diethyl Sulphide.—Plots of $k_{obs.}/[SEt_2]$ against $[SEt_2]/[Cl^-]$ are shown in Figures 2 and 3 for different experimental conditions. In this case only a more limited interval of $[SR_2]/[Cl^-]$ values could be explored since the reaction rate soon became too fast to be followed with our technique.



SCHEME 1

The curve-fitting procedure using the empirical expression (1) indicated that the ux^2 term is small and consequently the simplified expression (3) fits the kinetic data within the limits of experimental error. For this reason a reliable value cannot be given for the single constants k_2 and K_2 but only their product, k_2K_2, could be evaluated with sufficient accuracy.

$$k_{obs.}/[SR_2] = (rx + sx^2)/(1 + tx) \qquad (3)$$

Also in this case, the best-fitting procedure gave reliable values of r and s provided that the value of t was determined independently; this was done as in the SMe_2 case.

The values of k_1, K_1, and k_2K_2 obtained at different values of ionic strength and water content are reported in Table 5.

Reaction with Di-isopropyl Sulphide.—The plot of $k_{obs.}/[SPr^i_2]$ against $[SPr^i_2]/[Cl^-]$ is given in Figure 2. The curve-fitting procedure using equation (1) indicated that in this case both sx^2 and ux^2 terms are small and even the over-simplified equation (4) would nearly fit the kinetic data within the limits of experimental error. For this reason the given value of k_2K_2 is affected by a large degree of uncertainty.

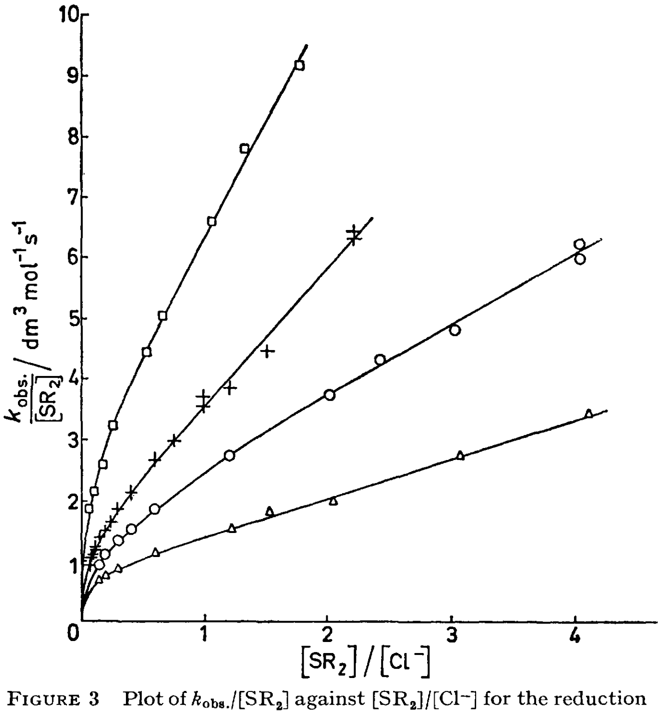


FIGURE 3 Plot of $k_{obs.}/[SR_2]$ against $[SR_2]/[Cl^-]$ for the reduction of gold(III) chloride by SEt_2 at I = 0.047 mol dm^{-3} ($Li[ClO_4]$) and 2 (△), 5 (○), and 10% (□) water in methanol, and at I = 0.106 mol dm^{-3} ($Li[ClO_4]$) and 5% water in methanol (+)

$$k_{obs.}/[SR_2] = rx/(1 + tx) \qquad (4)$$

Also in this case, the value of t was determined independently from spectrophotometric study of the substitution equilibrium.

The values of k_1, K_1, and k_2K_2 are reported in Table 4.

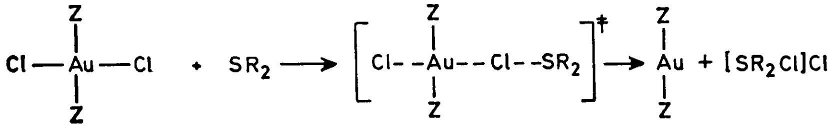
DISCUSSION

Several mechanisms may be invoked to account for the redox reaction which takes place through a bimolecular process involving a gold(III) substrate and a thioether molecule.

A bimolecular attack at the metal with formation of a substitution product which immediately undergoes an internal redox process can be ruled out since we have shown that the substitution reactions are faster than the reduction process, and that either the mono- or the bis-adduct needs an extra molecule of thioether in order to undergo the redox step.

Further, the addition of the sulphide to the four-co-ordinate substrate with formation of a reactive intermediate of higher co-ordination number can be considered unlikely, at least under our experimental conditions; since, if nucleophilic attack to the metal atom was the route to the redox step, then the same properties of the sulphide which favour substitution would also favour reduction. Comparison of K_1 in the three cases examined indicates that formation of the monosubstituted complex is favoured by less bulky sulphides; on the contrary, comparison of the k_1 values indicates that the redox step is favoured by the more basic (and also more bulky) sulphides. Therefore, since the steric effects appear to play an important role in the substitution process while electronic effects seem to be more important in the redox step, we conclude that nucleophilic attack at the metal is not the rate-determining step.

An atom-transfer redox process in which a chlorine atom is transferred from gold(III) to sulphide, leaving an electron pair on the metal, appears to be most likely and is depicted in Scheme 2. The cleavage of the terminal Au–Cl bond has been assumed to accompany the transfer of the chloride from Au to SR_2; this leads directly to a digonal gold(I) complex and to a $[SR_2Cl]Cl$ salt as primary reaction product. We did not detect the $[SR_2Cl]Cl$ salt in the reaction solution, but n.m.r. experiments showed that on dissolving either $[AuCl_3(SMe_2)]$ or $[SMe_2Br]Br$ in deuteriomethanol, $[SMe_2(OMe)]^+$ was formed in both cases; moreover in the presence of water, $[SMe_2(OMe)]^+$ readily evolves SMe_2O.[11]



$Z = Cl^-$ or SR_2

SCHEME 2

This reaction scheme is strongly reminiscent of the two-electron reduction of platinum(IV) complexes occurring through a single halide-bridge transfer; in both cases, in fact, not only the oxidation number but also the co-ordination number of the metal decreases by two units.

The hypothesis of a bimolecular attack at the chlorine and not at the metal centre is also in accord with the absence of significant steric effects in the redox rate-determining step.

It is very likely that also in the reduction of gold(III) halide by thiomorpholine [2] a chloride and not a hydroxyl group [of a hydrolysed gold(III) species] was transferred from gold to sulphur leaving a pair of electrons on the metal. We have shown, in fact, that the mass law retardation produced by added chloride has to be ascribed to shifts in the substitution equilibria and not to the suppression of the hydrolysis; once allowance for this is made, changes of hydrogen- and chloride-ion concentration are without effect on the reaction rate.

Comparison of k_0, k_1, and k_2 for a given sulphide would give the sequence of reactivity of $[AuCl_4]^-$, $[AuCl_3(SR_2)]$, and $[AuCl_2(SR_2)_2]^+$ respectively. All the three thioethers gave negligible values of k_0, and k_1 and k_2 could be determined with sufficient accuracy only in the SMe_2 case where k_2 was found to be 13 times larger than k_1. This indicates that the reactivity increases very sensibly with the positive charge of the substrate and hence with the electron affinity of the central metal.[12]

Comparison of either k_1 or k_2 values in the three sulphides would give the sequence of reducing power of the thioether. The relative ratios of k_1 values were 1 : 2.6 : 7.2 for SMe_2, SEt_2, and SPr^i_2 respectively, indicating that the reducing power increases with increasing σ-donor ability of the dialkyl sulphides; on the other hand, their steric hindrance is without noticeable effect.

Experiments at different ionic strengths and water content were performed in the SEt_2 case. The limited number of data available does not allow a discussion of the ionic-strength effect on a quantitative basis, although we observed an increase of the overall reaction rate with increasing ionic strength (Figure 3). This is in accord either with an increase of the redox kinetic constants (mainly k_2) or with an increase of the substitution equilibrium constant K_2; it is to be noted, in fact, that either in the redox or in the second substitution process, oppositely charged species are formed.

The reaction rate was also affected by the percentage of water in the methanolic solvent. Approximately linear plots were obtained for log k_1 and log k_2K_2 * against the percentage of water, which is proportional to solvent polarity.[13-15] This solvent dependence is in accord with the proposed redox mechanism, for with increasing solvent polarity the highly polar reaction products are expected to be more strongly solvated and the increased stability of these could be shared, to a large degree, by the transition state.

This study gives the first exhaustive description of the mechanism of reduction of gold(III) chloride by dialkyl sulphides in protic solvents, and shows, for the first time, that the mechanistic behaviour of gold(III) and platinum(IV) in complementary redox reactions can be strictly analogous.

The authors are grateful to Consiglio Nazionale delle Ricerche (C.N.R.), Rome, for support.

[9/619 *Received, 19th April,* 1979]

---

* K_2, like K_1, probably does not change appreciably in the three cases and therefore changes of log k_2K_2 are to be ascribed to changes of log k_2.

REFERENCES

[1] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley, New York, 1967.
[2] D. De Filippo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1971, **5**, 103.
[3] R. Roulet, N. Quang-Lan, W. R. Mason, and G. P. Fenske, jun., *Helv. Chim. Acta*, 1973, **56**, 2405.
[4] B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta*, 1976, **17**, 21; **20**, 43.
[5] V. M. Schul'man, Z. A. Savel'eva, and R. I. Novoselov, *Russ. J. Inorg. Chem.*, 1973, **18**, 376.
[6] A. Peloso, *Co-ordination Chem. Rev.*, 1977, **16**, 95.
[7] E. Bordignon, L. Cattalini, G. Natile, and A. Scatturin, *J.C.S. Chem. Comm.*, 1973, 878; G. Natile, E. Bordignon, and L. Cattalini, *Inorg. Chem.*, 1976, **15**, 246.
[8] P. C. Ray and D. C. Sen, *J. Indian Chem. Soc.*, 1930, **7**, 67.
[9] N. J. Leonard and C. R. Johnson, *J. Amer. Chem Soc.*, 1962, **84**, 3701.
[10] H. Bohme and E. Ball, *Z. anorg. Chem.*, 1957, **290**, 17.
[11] S. G. Smith and S. Winstein, *Tetrahedron*, 1958, **3**, 317.
[12] A. Peloso, G. Dolcetti, and R. Ettorre, *Inorg. Chim. Acta*, 1967, **1**, 403.
[13] P. Bickart, R. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.
[14] A. Peloso and M. Basato, *Co-ordination Chem. Rev.*, 1972, **8**, 111.
[15] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.