Kinetics and Mechanism of the Reaction between Tetrachloro- and Tetrabromo-aurate(III) and Thiocyanate

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The kinetics and mechanism for the overall reaction (i) (X = Cl or Br) have been studied at 25.0 °C using stopped-

$$3[\mathrm{AuX_4}]^- + 7\mathrm{SCN}^- + 4\mathrm{H_2O} \longrightarrow 3[\mathrm{Au(SCN)_2}]^- + \mathrm{HSO_4}^- + \mathrm{HCN} + 12\mathrm{X}^- + 6\mathrm{H}^+ \qquad \text{(i)}$$

flow spectrophotometry. The reaction takes place in two kinetically well separated steps. The initial, rapid process can be identified as stepwise ligand substitutions (ii) (n = 0—3) which take place *via* direct ligand dis-

$$[\mathrm{AuX}_{4-n}(\mathrm{SCN})_n]^- + \mathrm{SCN}^- \rightleftharpoons [\mathrm{AuX}_{3-n}(\mathrm{SCN})_{n+1}]^- + \mathrm{X}^- \qquad \text{(ii)}$$

placements, the solvent path being negligible. The substitution kinetics give no evidence for formation of persistent five-co-ordinate intermediates. The subsequent slower reaction is due to reduction of gold(III) to gold(I) thiocyanato-species. The rate of this step varies by four orders of magnitude within the accessible concentration interval of gold (10^{-6}—10^{-2} mol dm^{-3}). At high gold concentrations the reduction is slow and follows no simple-order kinetics due to inhibition by the cyanide formed as a product. This inhibition is eliminated for gold concentrations less than 5×10^{-6} mol dm^{-3}, where the redox reaction is rapid and strictly first order with respect to the concentrations of thiocyanate and gold complex. The mechanism for the reductive elimination is intermolecular involving a reaction between the gold(III) complex and an outer-sphere thiocyanate. Rate constants for reduction of $[\mathrm{AuBr_4}]^-$ and $[\mathrm{Au(SCN)_4}]^-$ by thiocyanate at 25 °C are $(5 \pm 2) \times 10^4$ and $(2.4 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1} respectively, for a 1.00 mol dm^{-3} perchlorate medium.

As long ago as 1918, Bjerrum and Kirschner[1] showed that both gold(III) and gold(I) thiocyanato-complexes are spontaneously reduced to metallic gold in aqueous solution. In particular, they studied the stoicheiometry and kinetics of the redox process (1) which was a

$$3[\mathrm{Au(SCN)_4}]^- + 4\mathrm{H_2O} \longrightarrow 3[\mathrm{Au(SCN)_2}]^- + 5\mathrm{HSCN} + \mathrm{HCN} + \mathrm{H_2SO_4} \qquad (1)$$

relatively slow reaction with a half-life of the order of hours and with no simple-order kinetics with respect to gold under the experimental conditions used. To prepare the tetrathiocyanatoaurate(III) complex, these authors used reaction (2) (X = Cl) between tetrachloroaurate(III) and thiocyanate, which was complete within the time of mixing.

$$[\mathrm{AuX_4}]^- + 4\mathrm{SCN}^- \rightleftharpoons [\mathrm{Au(SCN)_4}]^- + 4\mathrm{X}^- \qquad (2)$$

Very little has been published on gold thiocyanato-complexes since this classical paper. A few thermodynamic studies[2-5] have confirmed or only slightly revised the conclusions of the earlier workers about stabilities and standard potentials. Some qualitative observations were made[2,3] on the reduction rates of $[\mathrm{Au(SCN)_4}]^-$ according to (1), and a kinetic study of the reduction of tetrabromoaurate(III) by thiocyanate has been reported.[6] The latter gave no mechanistic information, however. In another, more recent, investigation[7] of the $[\mathrm{AuCl_4}]^-$–thiocyanate reaction, two consecutive processes were observed on the stopped-flow time scale. The initial rapid change was interpreted as formation of a persistent five-co-ordinate intermediate $[\mathrm{AuCl_4} \cdots \mathrm{SCN}]^{2-}$, and the subsequent, slower, process as the decay of the intermediate to $[\mathrm{AuCl_3(SCN)}]^-$ and chloride. This interpretation is not in accordance with the results reported here. The present paper continues our earlier studies[8,9] on gold(III) complexes.

SURVEY OF THE SYSTEM

For gold concentrations less than *ca.* 5×10^{-6} mol dm^{-3} the concentration of cyanide formed in the reduction (1) is so small that formation of gold(III) cyano-complexes in acidic solutions can be neglected. Combination of reactions (1) and (2) gives the overall reaction (3) (X = Cl or Br).

$$3[\mathrm{AuX_4}]^- + 7\mathrm{SCN}^- + 4\mathrm{H_2O} \longrightarrow 3[\mathrm{Au(SCN)_2}]^- + \mathrm{HSO_4}^- + \mathrm{HCN} + 12\mathrm{X}^- + 6\mathrm{H}^+ \qquad (3)$$

Addition of excess of thiocyanate to solutions of $[\mathrm{AuCl_4}]^-$ or $[\mathrm{AuBr_4}]^-$ with gold concentrations less than 5×10^{-6} mol dm^{-3} reveals two kinetically well separated reactions. For $c_{\mathrm{Au}} < 10^{-5}$ mol dm^{-3}, both these reactions are strictly first order with respect to the thiocyanate concentration. The initial fast step can be identified as consecutive substitutions of halide ligands by thiocyanate, and the subsequent process as a reduction of gold(III) complexes to $\mathrm{Au^I}$. Both reactions have half-lives within the stopped-flow region, but the substitution is always at least ten times faster than the reduction, so they can be studied independently of each other.

Ligand-substitution Equilibria.—The equilibrium constants (4) (n = 0—3; X = Cl or Br) for the stepwise processes (5) are related to the overall stability constants

$$K_n = [\mathrm{AuX}_{3-n}(\mathrm{SCN})_{n+1}{}^-][\mathrm{X}^-]/[\mathrm{AuX}_{4-n}(\mathrm{SCN})_n{}^-][\mathrm{SCN}^-] \qquad (4)$$

$$[\mathrm{AuX}_{4-n}(\mathrm{SCN})_n]^- + \mathrm{SCN}^- \rightleftharpoons [\mathrm{AuX}_{3-n}(\mathrm{SCN})_{n+1}]^- + \mathrm{X}^- \qquad (5)$$

$$\beta_{4\mathrm{X}} = [\mathrm{AuX_4}^-]/[\mathrm{Au}^{3+}][\mathrm{X}^-]^4 \qquad (6)$$

$$K_0K_1K_2K_3 = \beta_{4\mathrm{SCN}}/\beta_{4\mathrm{X}} = \frac{[\mathrm{Au(SCN)_4}^-]}{[\mathrm{AuX_4}^-]}\left(\frac{[\mathrm{X}^-]}{[\mathrm{SCN}^-]}\right)^4 \qquad (7)$$

(6) for the simple systems by equation (7). Skibsted and Bjerrum [10] have calculated $\beta_{4Cl} = 10^{26}$, $\beta_{4Br} = 10^{34}$, and $\beta_{4SCN} = 10^{45}$ dm^{12} mol^{-4}. From these values and equation (7) it follows immediately[11] that $[Au(SCN)_4]^-$ probably was the predominant reaction product in the fast substitution process observed in the previous study by Hall and Satchell,[7] not $[AuCl_3(SCN)]^-$ as suggested by these authors {$[Au(SCN)_4^-]/[AuCl_4^-] > 10^8$ for the large $[SCN^-]/[Cl^-]$ values ($>3 \times 10^{-3}$) used}.

Spectra.—Figure 1 shows spectra of solutions containing equilibrium mixtures of the short-lived complexes $[AuX_{4-n}(SCN)_n]^-$ (n = 0—4) recorded using a continuous-flow cell before any significant reduction to Au^I has occurred. It follows from the values of β_{4Cl}, β_{4Br}, and β_{4SCN} given above that even at the lowest $[SCN^-]/[X^-]$ value (5×10^{-5}) most of the gold will probably be present as $[AuCl(SCN)_3]^-$ and $[Au(SCN)_4]^-$ in the chloro–thiocyanato-system, whereas in the bromo–thiocyanato-system various mixed complexes $[AuBr_{4-n}(SCN)_n]^-$ (n = 0—4) will probably contribute to the overall absorbance. The limiting curve for high concentrations of thiocyanate can be identified as the spectrum for $[Au(SCN)_4]^-$.[12] The rapid increase of absorbance observed at 312 nm (the wavelength also used in ref. 7) is therefore due to the stepwise substitutions (5).

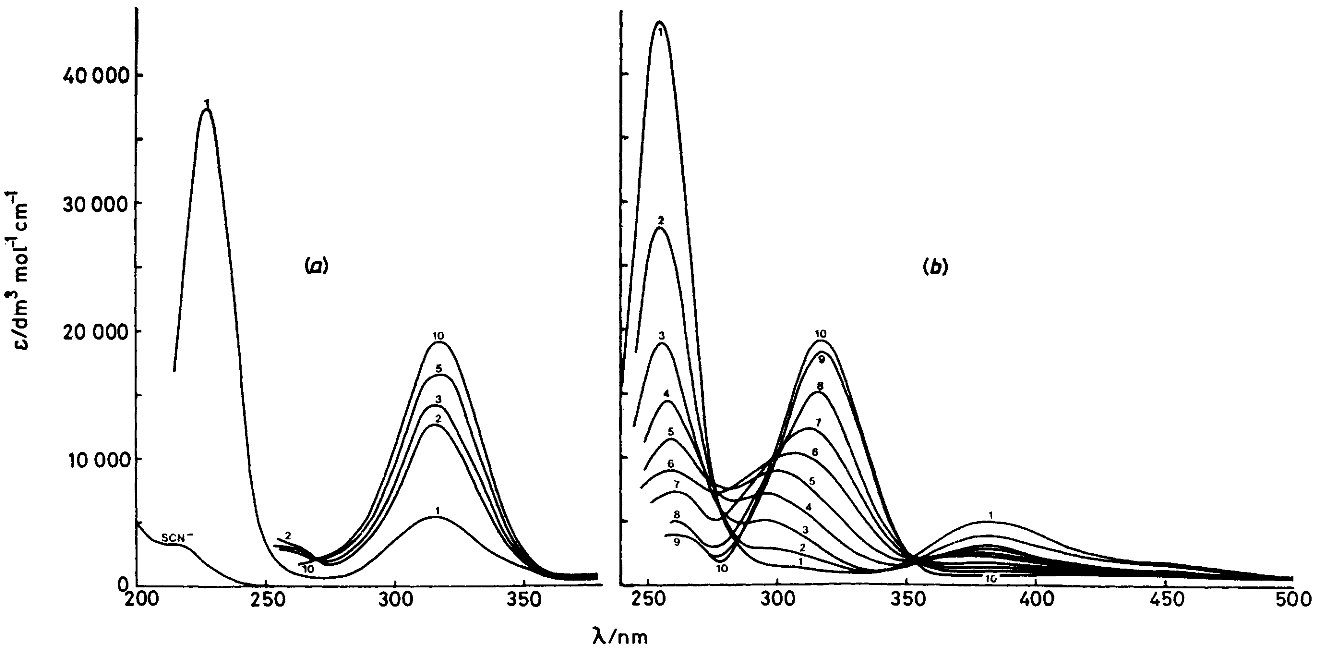


FIGURE 1 Spectra of solutions containing equilibrium mixtures of the short-lived complexes $[AuX_{4-n}(SCN)_n]^-$ [n = 0—4; X = Cl (*a*) or Br (*b*)], recorded on a continuous-flow system before any significant reduction to Au^I has occurred. In (*a*): c_{SCN} = 0 (1), 0.05 (2), 0.2 (3), 1.0 (5), and 100 (10) mmol dm^{-3}; c_{Cl} = 1 000 (1,2,3), 500 (5), and 10 (10) mmol dm^{-3}. In (*b*): c_{SCN} = 0 (1), 0.05 (2), 0.2 (3), 0.6 (4), 1.0 (5—9), and 100 (10) mmol dm^{-3}; c_{Br} = 1 000 (1—4), 500 (5) 175 (6), 62.5 (7), 7.5 (8), 3.0 (9), and 1.0 (10) mmol dm^{-3}

Substitution Kinetics.—The experiments indicate that Scheme 1 can be used to describe the overall process (2), *cf.* the analogous $[AuCl_4]^-$–Br$^-$ and $[PtCl_4]^{2-}$–Br$^-$ systems.[8,13] The large difference in *trans* effect between halides and thiocyanate makes negligible the reaction *via* the *cis* isomer. Because of the subsequent rapid redox process, it has been possible to study only some of the stepwise substitutions indicated in the Scheme, *viz.* reactions (8)—(10).

$$[AuBr_4]^- + SCN^- \rightleftharpoons [AuBr_3(SCN)]^- + Br^- \quad (8)$$

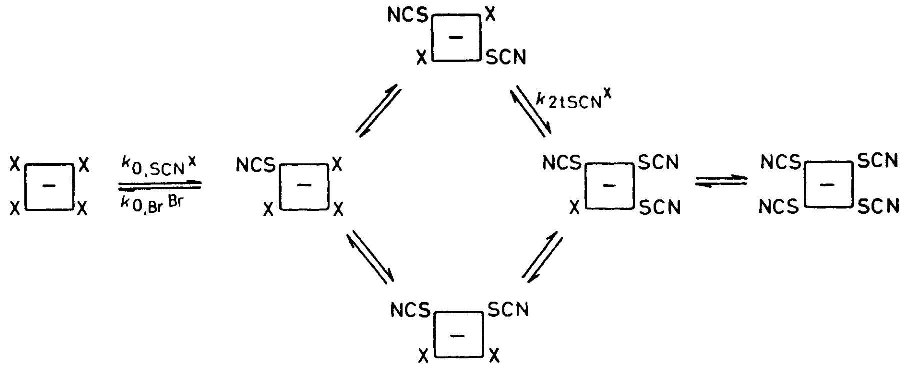
$$trans\text{-}[AuBr_2(SCN)_2]^- + SCN^- \longrightarrow [AuBr(SCN)_3]^- + Br^- \quad (9)$$

$$[AuCl_4]^- + SCN^- \longrightarrow [AuCl_3(SCN)]^- + Cl^- \quad (10)$$

Redox Kinetics.—The redox reaction can be followed as a decrease of absorbance at 312 nm where all the reaction products in equation (3) have negligible absorbance compared to the $[AuX_{4-n}(SCN)_n]^-$ complexes, *cf.* Figure 1.

The redox rate varies over about four orders of magnitude with the total concentration of gold(III) for $c_{Au} > 5 \times 10^{-6}$ mol dm^{-3}. This is illustrated in Figure 2, where the redox rate constants (or estimated constants, when the kinetics deviate from first order) from various studies have been plotted against c_{Au} on a logarithmic scale. This large variation in rate has been overlooked in previous studies. The kinetics deviate from simple first order for $c_{Au} >$ *ca.* 10^{-5} mol dm^{-3}. The deviations are very large for the high gold concentrations that were used in the early study by Bjerrum and Kirschner (see ref. 1, p. 8). The variation of the rate constants with gold concentration is also evident in the plots in Figure 3, where the curves for 1.25×10^{-5} and 5×10^{-5} mol dm^{-3} gold(III) deviate from the two at smaller gold(III) concentrations.

This strong gold(III) dependence cannot be explained as due to inhibition by the Au^I formed. The reduction is rapid and complete for $c_{Au} \leqslant 5 \times 10^{-6}$ mol dm^{-3}. The experiments in Table 1 show that addition of cyanide-free $[Au(SCN)_2]^-$ prepared by reduction of $[AuCl_4]^-$ with sulphite and subsequent addition of thiocyanate does not change the rate constants. On the other hand, addition of cyanide



SCHEME 1 Reaction model for the substitutions. The reaction *via* the *cis* isomer is negligible because thiocyanate has a much larger *trans* effect than chloride and bromide

to the reaction mixture strongly inhibits the reaction * and causes deviations from first-order kinetics. Gold(I) prepared according to (3) by reduction of $[AuCl_4]^-$ (c_{Au} > 10^{-5} mol dm^{-3}) with thiocyanate has a similar effect, since these solutions contain cyanide, *cf.* Table 1.

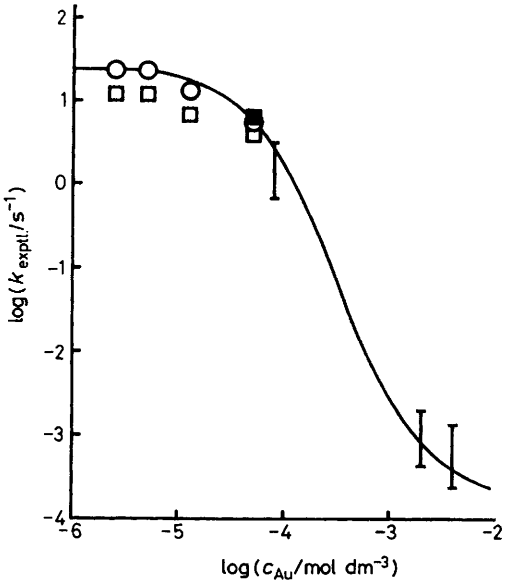


FIGURE 2 Observed rate ' constant ' for the reduction plotted as a function of c_{Au} on a logarithmic scale. $c_{Au} = 2.5 \times 10^{-6}$, 5×10^{-6}, 1.25×10^{-5} and 5×10^{-5} mol dm^{-3} with $c_{SCN} = 0.100$ (○) or 0.01 mol dm^{-3} (□), $c_{Cl} = 0.100$ mol dm^{-3}, and $[H^+] =$ 10 mmol dm^{-3}. The value from ref. 7 for $c_{Au} = 4 \times 10^{-5}$ mol dm^{-3}, $c_{SCN} = 10$ mmol dm^{-3}, $c_{Cl} = 0.100$ mol dm^{-3}, and $[H^+] =$ 2 mmol dm^{-3} (■) and estimated values from ref. 6 for $c_{Au} \approx 8 \times 10^{-5}$ mol dm^{-3} and $c_{SCN} = 10$ mmol dm^{-3} and from ref. 1 with $c_{Au} \approx 2 \times 10^{-3}$ or 4×10^{-3} mol dm^{-3}, $c_{SCN} \approx 100$ mmol dm^{-3} are also shown

From these observations we conclude that the cyanide formed in the redox process (3) inhibits the reaction, probably by rapid co-ordination to Au^{III}. Even for large concentrations of Au^{III} (10^{-4}—10^{-3} mol dm^{-3}), kinetic experiments show a very fast initial reduction of some of the gold. The cyanide formed during this initial period can rapidly co-ordinate to the unchanged Au^{III}, causing a gradual decrease of the reduction rate and deviations from first-order kinetics. [Gold(III)–cyanide complexes are reduced very slowly by thiocyanate.]

For the small concentrations of gold used in the present study ($c_{Au} < 5 \times 10^{-6}$ mol dm^{-3}) this effect of cyanide is eliminated. The equilibrium constant for reaction (11)

$$4HCN + [Au(SCN)_4]^- \rightleftharpoons [Au(CN)_4]^- + 4H^+ + 4SCN^- \quad (11)$$

is approximately 1 ($\beta_{4CN}/\beta_{4SCN} \approx 10^{37}$, *cf.* ref. 10 and p$K_a$ = 9.4 for HCN). For the experimental conditions given in Table 3, the quotient $[Au(CN)_4^-]/[Au(SCN)_4^-]$ will therefore be small except for the lowest concentrations of thiocyanate used. In addition, the rate of substitution of thiocyanate by cyanide in $[Au(SCN)_4]^-$ will probably be small compared to the reduction rate for total cyanide concentration less than 10^{-6} mol dm^{-3} which corresponds to a concentration of free cyanide ions of less than 10^{-11} mol dm^{-3} at the pH used.

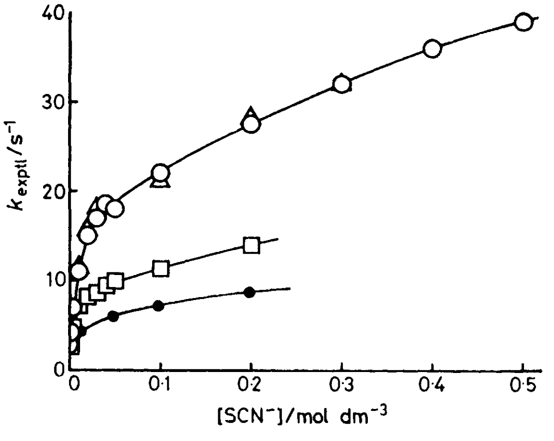


FIGURE 3 Plot of the observed rate constant for the reduction of $[AuCl_4]^-$ against the thiocyanate concentration at large concentrations of thiocyanate. $c_{Cl} = 0.100$; $c_{Au} = 2.5 \times 10^{-6}$, (△), 5×10^{-6} (○), 1.25×10^{-5} (□), or 5×10^{-5} mol dm^{-3} (●)

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* Bjerrum and Kirschner (ref. 1, p. 16) also observed that cyanide influences the redox rate. They reported a rapid decolouration of the $[Au(SCN)_4]^-$ solution, when excess of cyanide was added. The change was assumed to be due to a rapid reduction, but is more probably caused by rapid formation of $[Au(CN)_4]^-$.

TABLE 1

Variation of the reduction rate constant with the concentrations of $[AuCl_4]^-$, Au^I, and CN^-

$10^3[SCN^-]$	$10^6[AuCl_4^-]$			
mol dm^{-3}		pH	$k_{exptl.}/s^{-1}$	Added substance [a]
50	5.0	2.0	18 ± 2	$[Au(SCN)_2]^-$ [a] (6.5×10^{-4})
50	5.0	2.0	18 ± 2	
100	5.0	2.0	21 ± 2	$[Au(SCN)_2]^-$ [b] (6.5×10^{-4})
100	5.0	2.0	22 ± 2	
300	5.0	2.0	23 ± 2	$[Au(SCN)_2]^-$ [b] (6.5×10^{-4})
300	5.0	2.0	24 ± 2	
50	1.0	3.0	15 ± 2	Au^I [c] (1.0×10^{-5})
50	5.0	2.0	2.1 ± 0.2	Au^I [c] (3.5×10^{-4})
465	5.0	2.0	1.8 ± 0.2	Au^I [c] (3.5×10^{-4})
500	1.0	*ca.* 9	*d*	Na[CN] (1.0×10^{-4})
100	1.0	*ca.* 9	9 ± 1	Na[CN] (2.5×10^{-5})
100	1.0	*ca.* 8	17 ± 3	Na[CN] (1.0×10^{-5})

[a] Concentrations (mol dm^{-3}) are given in parentheses. [b] Prepared by reduction of $[AuCl_4]^-$ with HSO_3^- and subsequent addition of excess of Na[SCN]. [c] Prepared by reduction of $[AuCl_4]^-$ with SCN^- according to reaction (3). [d] No reduction.

EXPERIMENTAL

Chemicals and Solutions.—Hydrogen tetrachloroaurate(III) trihydrate, $HAuCl_4 \cdot 3H_2O$ (Mallinckrodt or Degussa), was used directly. Stock solutions (1.00 mol dm^{-3}) were prepared from perchloric acid, sodium perchlorate (Baker *p.a.*), sodium chloride (Merck *p.a.*), sodium bromide, and sodium thiocyanate (Mallinckrodt *p.a.*) using water doubly distilled from quartz vessels. Stock solutions of potassium cyanide (B.D.H. *p.a.*) were 0.010 mol dm^{-3}.

Solutions of tetrabromoaurate(III) were prepared by addition of NaBr to solutions of tetrachloroaurate(III) in concentrations such that $[Br^-]/[Cl^-] \geqslant 10$ (*cf.* ref. 8). Gold(I) solutions were prepared either by reduction of $[AuCl_4]^-$ with excess of thiocyanate according to equation (3), or by reduction of $[AuCl_4]^-$ with a 5% deficit of sodium hydrogensulphite (Merck *p.a.*) and subsequent rapid addition of excess of thiocyanate.

Stoicheiometry.—The stoicheiometry of reaction (1) was carefully studied by Bjerrum and Kirschner.[1] Gravimetric sulphate analyses for the small concentrations of gold ($< 5 \times 10^{-5}$ mol dm^{-3}) used in the present study showed that $[Au^{III}]/[\text{sulphate}]$ was 3.0 ± 0.1 in agreement with ref. 1. After reduction, the Au^I will be present as $[Au(SCN)_2]^-$ under the experimental conditions used [*cf.* the stability constants for gold(I) complexes given by Skibsted and Bjerrum [10] and $pK_a(HCN) = 9.40$].

Spectra.—The spectra in Figure 1 were recorded using a Beckman model 25 recording instrument. A continuous-flow system consisting of a Hellma QS-178 2-cm flow cell equipped with a mixer and having a dead-time < 20 ms, much smaller than the redox half-lives of the gold(III) complexes, was used.

Kinetics.—All reactions were started by mixing equal volumes of a metal solution (M) and a ligand solution (L) at 25.00 ± 0.02 °C. The change of absorbance at 312 nm was followed using a modified Durrum–Gibson stopped-flow instrument. The absorbance first increases rapidly due to the substitutions (5) and then slowly decreases due to the reduction (*cf.* Figure 1). The metal solution (M) contained gold(III) ($c_{Au} \leqslant 1.0 \times 10^{-5}$ mol dm^{-3}) and various concentrations of chloride or bromide. The ligand solution (L) contained thiocyanate and in experiments with large halide concentrations, chloride or bromide also. For the experiments in Table 1, the solution of L contained Au^I or cyanide also.

Tables 1—3 give the concentrations after mixing, all solutions having an ionic strength of 1.00 mol dm^{-3} with sodium perchlorate as the supporting electrolyte. The hydrogen-ion concentration was varied within the interval $0.2 \leqslant [H^+] \leqslant 20$ mol dm^{-3} by substitution of part of the $Na[ClO_4]$ of the metal solution by perchloric acid. This variation had no influence on the reaction rates. The formation of HSCN was negligible ($pK_a = -1.8$).[14] For $[H^+] > 0.1$ mol dm^{-3} side reactions due to decomposition of thiocyanate disturb the kinetics.

Large excesses of thiocyanate, chloride, bromide, gold(I), or cyanide compared to gold(III) complex gave pseudo-first-order kinetics. Reverse processes were negligible, except for reaction (8). Rate constants were calculated from first-order rate expressions using a least-squares program and a computer.

Substitution.—The experiments are summarized in Table 2. The reversible reaction (8) was started by mixing a metal solution having $c_{Au} = 1 \times 10^{-5}$, $c_{Br} = 0.990$ or 0.500, and $[H^+] = 0.010$ mol dm^{-3} with ligand solutions containing either sodium thiocyanate (0.10, 0.15, 0.20, 0.30, 0.40, 0.50, 0.80, or 1.2 mmol dm^{-3}) in 1.00 mol dm^{-3} NaBr or sodium thiocyanate (0.10, 0.15, 0.20, 0.30, 0.40, or 0.50 mmol dm^{-3}) in 1.00 mol dm^{-3} NaBr or $Na[ClO_4]$. The reaction product in these runs was mainly $[AuBr_3(SCN)]^-$.

Reaction (9) was followed by mixing a ligand solution having c_{SCN} 2.0, 4.0, or 8.0 mmol dm^{-3} and $[H^+] = 2.0$ mmol dm^{-3} with a metal solution containing 1×10^{-5} mol dm^{-3} $[AuBr_3(OH)]^-$ in 1.00 mol dm^{-3} $Na[ClO_4]$. The metal solution was prepared by addition of 1 equivalent of sodium hydroxide to a 0.1 mmol dm^{-3} $[AuBr_4]^-$ solution in 1.00 mol dm^{-3} $Na[ClO_4]$. After mixing, the reactions (12) take place. The preceding fast reactions are complete within less than one half-life of the slow process, and the subsequent reaction $[AuBr(SCN)_3]^- \longrightarrow [Au(SCN)_4]^-$ is fast because of the large *trans* effect of thiocyanate compared to bromide.

$$[AuBr_3(OH)]^- \xrightarrow[\text{Fast}]{+H^+} [AuBr_3(OH_2)] \xrightarrow[\text{Fast}]{+SCN^-}$$
$$[AuBr_3(SCN)]^- \xrightarrow[\text{Fast}]{+SCN^-}$$
$$trans\text{-}[AuBr_2(SCN)_2]^- \xrightarrow[\text{Slow}]{+SCN^-} [AuBr(SCN)_3]^- \xrightarrow[\text{Fast}]{+SCN^-}$$
$$[Au(SCN)_4]^- \quad (12)$$

Reaction (10) was followed by mixing a metal solution

TABLE 2

Substitution kinetics of reactions (8)—(10). Wavelength 312 nm, $c_{\mathrm{Au}} = 5 \times 10^{-6}$, $[\mathrm{H}^+] = 5 \times 10^{-3}$ mol dm^{-3}

Reaction	$10^4[\mathrm{SCN}^-]$	$[\mathrm{X}^-]$	$k_{\mathrm{exptl.}}/\mathrm{s}^{-1}$
	mol dm^{-3}		
(8) X = Br	0.50	0.995	18 ± 1
	0.75	0.995	21 ± 1
	1.0	0.995	22 ± 1
	1.5	0.995	27 ± 1
	2.0	0.995	34 ± 2
	2.5	0.995	37 ± 2
	4.0	0.995	49 ± 2
	6.0	0.995	63 ± 3
	0.50	0.750	16 ± 1
	0.75	0.750	19 ± 1
	1.0	0.750	19 ± 1
	1.5	0.750	25 ± 1
	2.0	0.750	29 ± 1
	2.5	0.750	34 ± 1
	0.50	0.495	12 ± 1
	0.75	0.495	13 ± 1
	1.0	0.495	15 ± 1
	1.5	0.495	20 ± 1
	2.0	0.495	24 ± 2
	2.5	0.495	28 ± 2
(9) X = Br	10.0		10 ± 2
	20.0		22 ± 2
	40.0		46 ± 3
(10) X = Cl	5.0	0.100	8 ± 1
	10.0	0.100	14 ± 1
	20.0	0.100	25 ± 2
	30.0	0.100	40 ± 3
	40.0	0.100	52 ± 5
	50.0	0.100	67 ± 7

having $c_{\mathrm{Au}} = 1 \times 10^{-5}$, $c_{\mathrm{Cl}} = 2.00$, and $[\mathrm{H}^+] = 0.020$ mol dm^{-3} with ligand solutions of sodium thiocyanate (1.0, 2.0, 4.0, 6.0, 8.0, or 10.0 mmol dm^{-3}). After mixing, the reactions (13) take place. Reaction (10) can be observed as a

$$[\mathrm{AuCl_4}]^- \xrightarrow[\text{Slow}]{+\mathrm{SCN}^-} [\mathrm{AuCl_3(SCN)}]^- \xrightarrow[\text{Fast}]{+\mathrm{SCN}^-}$$

$$trans\text{-}[\mathrm{AuCl_2(SCN)_2}]^- \xrightarrow[\text{Slow}]{+\mathrm{SCN}^-}$$

$$[\mathrm{AuCl(SCN)_3}]^- \xrightarrow[\text{Fast}]{+\mathrm{SCN}^-} [\mathrm{Au(SCN)_4}]^- \quad (13)$$

fast initial process followed by the slower reaction between *trans*-$[\mathrm{AuCl_2(SCN)_2}]^-$ and thiocyanate. It may be disturbed by the subsequent slower reaction.

Redox Reactions.—The preliminary experiments in Table 1 and in Figures 2 and 3 show that simple first-order kinetics are obtained and the gold(III) dependence is eliminated for $c_{\mathrm{Au}} \leqslant 5 \times 10^{-6}$ mol dm^{-3}. The experiments summarized in Table 3 were performed at various constant $[\mathrm{SCN}^-]/[\mathrm{X}^-]$, X = Cl or Br, each having a constant distribution of the gold between the different gold(III) complexes, *cf.* equation (4). The metal solution contained $[\mathrm{AuCl_4}]^-$ and NaCl or $[\mathrm{AuBr_4}]^-$ and NaBr, and the ligand solution contained Na[SCN] in a chloride- or bromide-perchlorate medium.

The reaction for $\bar{n}_{\mathrm{SCN}} = 4$ [*] was started by mixing either a solution of sodium thiocyanate (2.0, 6.0, or 10.0 mmol dm^{-3}) with a solution of $[\mathrm{AuCl_4}]^-$ ($c_{\mathrm{Au}} = 1.0 \times 10^{-5}$, $c_{\mathrm{Cl}} = 0.200$ mol dm^{-3}, $[\mathrm{H}^+] = 20$ mmol dm^{-3}) or a solution of sodium thiocyanate (1.0, 2.0, 4.0, or 6.0 mmol dm^{-3}) with a solution of $[\mathrm{AuBr_4}]^-$ ($c_{\mathrm{Au}} = 1.0 \times 10^{-5}$, $c_{\mathrm{Br}} = 1 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{H}^+] = 10$ mmol dm^{-3}). The quotient $[\mathrm{SCN}^-]/[\mathrm{X}^-]$ was 0.01 (Cl$^-$) or $\geqslant 1$ (Br$^-$). The starting complex for the reduction in these runs was $[\mathrm{Au(SCN)_4}]^-$, *cf.* the stability constants $\beta_{4\mathrm{Cl}}$, $\beta_{4\mathrm{Br}}$, and $\beta_{4\mathrm{SCN}}$ given above and the spectra in Figure 1.

TABLE 3

Redox kinetics. $c_{\mathrm{Au}} = 5 \times 10^{-6}$, $[\mathrm{H}^+] = 5 \times 10^{-3}$ mol dm^{-3}; wavelength 312 nm

	$10^4[\mathrm{SCN}^-]/[\mathrm{X}^-]$	$10^3[\mathrm{SCN}^-]$	$10^3[\mathrm{X}^-]$	$k_{\mathrm{exptl.}}/\mathrm{s}^{-1}$
		mol dm^{-3}		
(*a*) $n_{\mathrm{SCN}} < 4$				
X = Cl	0.48	0.05	950	0.26 ± 0.02
	5.0	0.05	100	0.20 ± 0.02
	5.0	0.15	300	0.50 ± 0.05
	5.0	0.25	500	1.0 ± 0.1
	5.0	0.475	450	1.9 ± 0.3
	10.0	0.10	100	0.40 ± 0.03
	10.0	0.30	300	1.0 ± 0.2
	10.0	0.50	500	1.6 ± 0.2
	10.0	0.95	950	3.1 ± 0.3
X = Br	0.5	0.045	900	1.8 ± 0.2
	1.0	0.05	500	1.5 ± 0.2
	1.0	0.09	900	2.7 ± 0.2
	2.0	0.06	300	1.2 ± 0.1
	2.0	0.10	500	2.0 ± 0.2
	2.0	0.18	900	3.7 ± 0.3
	5.0	0.05	100	0.9 ± 0.1
	5.0	0.15	300	2.2 ± 0.2
	5.0	0.25	500	4.0 ± 0.5
	5.0	0.45	900	7.0 ± 1
	10	0.10	100	1.2 ± 0.3
	10	0.30	300	3.7 ± 0.5
	10	0.50	500	5.8 ± 0.5
	10	0.90	900	11 ± 1
	50	0.50	100	4.2 ± 0.5
	50	1.5	300	12.5 ± 0.5
	50	2.5	500	20 ± 1
	50	4.5	900	35 ± 3
	100	1.0	100	7.0 ± 1
	100	3.0	300	20 ± 2
	100	5.0	500	30 ± 3
	500	1.5	30	5.2 ± 0.5
	500	2.5	50	9 ± 1
	500	5.0	100	18 ± 1
	1 000	1.0	10	2.9 ± 0.3
	1 000	3.0	30	9 ± 1
	1 000	5.0	50	14 ± 2
	1 000	10	100	25 ± 3
(*b*) $n_{\mathrm{SCN}} = 4$				
X = Cl	100	1.0	100	2.7 ± 0.1
	100	2.0	200	4.8 ± 0.2
	100	3.0	300	7.5 ± 1.0
X = Br	$>1 \times 10^4$	0.5	0.5	1.3 ± 0.2
		1.0	0.5	2.1 ± 0.2
		2.0	0.5	4.7 ± 0.3
		3.0	0.5	7.2 ± 0.5

The reduction for $[\mathrm{SCN}^-] > 5$ mmol dm^{-3} (see Figure 3) was started by mixing a metal solution containing $c_{\mathrm{Au}} = 1 \times 10^{-5}$ or 5×10^{-6} and $c_{\mathrm{Cl}} = 0.200$ mol dm^{-3} with a ligand solution of sodium thiocyanate (0.020, 0.040, 0.060, 0.080, 0.100, 0.200, 0.400, 0.600, 0.800, or 1.000 mol dm^{-3}).

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[*] $\bar{n}_{\mathrm{SCN}}$ denotes the mean number of thiocyanate ligands bound to the metal ion.[11]

RESULTS AND DISCUSSION

Substitution.—The stepwise substitutions (8)—(10) take place *via* direct ligand exchanges. Similar to the $[AuCl_4]^-$–bromide system,[8] the solvent path is negligible. Using the notations for the rate constants in Scheme 1, the observed first-order rate constant for excess of thiocyanate and bromide for reaction (8) can be written as in (14). Figure 4(*a*) shows plots of the observed rate constant against the thiocyanate concentration at three different bromide concentrations. According to equation (14), the slopes give $k_{0,\mathrm{SCN}}{}^{\mathrm{Br}}$ and the intercepts $k_{0,\mathrm{Br}}{}^{\mathrm{Br}}[\mathrm{Br}^-]$. Figure 4(*b*) shows a plot of the intercept against $[\mathrm{Br}^-]$ which gives $k_{0,\mathrm{Br}}{}^{\mathrm{Br}}$ as the slope.

$$k_{\mathrm{exptl.}} = k_{0,\mathrm{SCN}}{}^{\mathrm{Br}}[\mathrm{SCN}^-] + k_{0,\mathrm{Br}}{}^{\mathrm{Br}}[\mathrm{Br}^-] \qquad (14)$$

Reactions (9) and (10) were studied using a large excess of thiocyanate so the reverse reactions were suppressed. The experimental rate constants are given by equations (15) and (16). Figure 4(*c*) and (*d*) show the corresponding plots the slopes of which gave $k_{2t,\mathrm{SCN}}{}^{\mathrm{Br}}$ and $k_{0,\mathrm{SCN}}{}^{\mathrm{Cl}}$, respectively.

$$k_{\mathrm{exptl.}} = k_{2t,\mathrm{SCN}}{}^{\mathrm{Br}}[\mathrm{SCN}^-] \qquad (15)$$

$$k_{\mathrm{exptl.}} = k_{0,\mathrm{SCN}}{}^{\mathrm{Cl}}[\mathrm{SCN}^-] \qquad (16)$$

The rate constants are given in Table 4 together with the statistically corrected values. A comparison of $k_{0,\mathrm{SCN}}{}^{\mathrm{Br}}$ and $k_{2t,\mathrm{SCN}}{}^{\mathrm{Br}}$ shows that the relative *cis* effect, $\mathrm{Br}^-/\mathrm{SCN}^-$, is about 2. The values for $k_{0,\mathrm{SCN}}{}^{\mathrm{Br}}$ and $k_{0,\mathrm{SCN}}{}^{\mathrm{Cl}}$ show that the relative *trans* effect, $\mathrm{Br}^-/\mathrm{Cl}^-$, is 8 for thiocyanate as entering ligand, which should be compared to the value (14) obtained previously[8] for chloride and bromide as entering ligands. Thus, the relative *trans* effect depends on the nature of the entering ligand for gold(III) complexes. This is valid for the platinum(II) complexes also.[15] The equilibrium constant $K_0 = k_{0,\mathrm{SCN}}{}^{\mathrm{Br}}/k_{0,\mathrm{Br}}{}^{\mathrm{Br}} = (6.2 \pm 0.7) \times 10^3$ for reaction (8) can also be obtained from the kinetics.

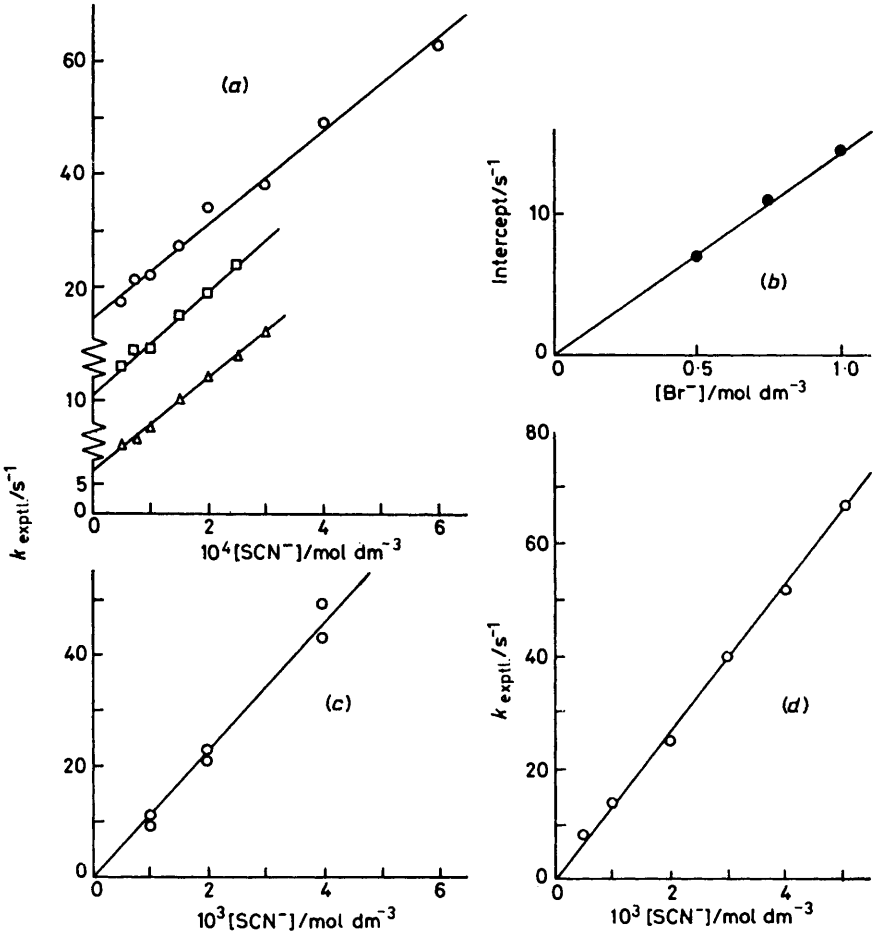


FIGURE 4 Plots of the observed rate constants against thiocyanate concentration for the substitution reactions (8) (*a*), (9) (*c*), and (10) (*d*). In (*a*), $[\mathrm{Br}^-] = 0.995$ (○), 0.750 (□), and 0.495 (△) mol dm^{-3}. In (*b*), the intercepts from (*a*) have been plotted against $[\mathrm{Br}^-]$

Reduction.—On the time scale of the redox process the ligand substitutions can be considered as rapid equilibria. For an intramolecular redox process the reduction rate should be independent of the concentration of free thiocyanate for constant distribution of gold between the various complexes $[AuX_{4-n}(SCN)_n]$ ($n = 0$—4). The distribution is determined by $[\mathrm{SCN}^-]/[\mathrm{X}^-]$, *cf.* equation

TABLE 4

Rate constants at 25 °C in 1.00 mol dm^{-3} perchlorate media. *m* is a statistical factor (the number of equivalent leaving ligands in the substitution reactions)

Reaction	Rate constant	k/dm^3 mol^{-1} s^{-1}	$\frac{k/m}{\mathrm{dm^3\ mol^{-1}\ s^{-1}}}$
(*a*) Substitution			
$[AuCl_4]^- + SCN^- \longrightarrow [AuCl_3(SCN)]^- + Cl^-$	$k_{0,SCN}^{Cl}$	*ca.* 1.3 × 10^4 *	0.3 × 10^4
$[AuBr_4]^- + SCN^- \longrightarrow [AuBr_3(SCN)]^- + Br^-$	$k_{0,SCN}^{Br}$	(8.7 ± 0.4) × 10^4	2.2 × 10^4
trans-$[AuBr_2(SCN)_2]^- + SCN^- \longrightarrow [AuBr(SCN)_3]^- + Br^-$	$k_{2,tSCN}^{Br}$	(1.2 ± 0.2) × 10^4	0.6 × 10^4
$[AuBr_3(SCN)]^- + Br^- \longrightarrow [AuBr_4]^- + SCN^-$	$k_{0,Br}^{Br}$	14 ± 1	14
(*b*) Reduction			
$[AuBr_4]^- + SCN^- \longrightarrow [AuBr_2]^- + Br^- + BrSCN$	$k_{r,0}^{Br}$	(5 ± 2) × 10^4	
$[Au(SCN)_4]^- + SCN^- \longrightarrow [Au(SCN)_2]^- + SCN^- + (SCN)_2$	$k_{r,4}^{X}$	(2.4 ± 0.2) × 10^3	

* The value of this rate constant may be influenced by the subsequent reaction between *trans*-$[AuCl_2(SCN)_2]^-$ and SCN$^-$.

(4). For an intermolecular process, on the other hand, the rate should be proportional to the concentration of free thiocyanate for constant [SCN$^-$]/[X$^-$].

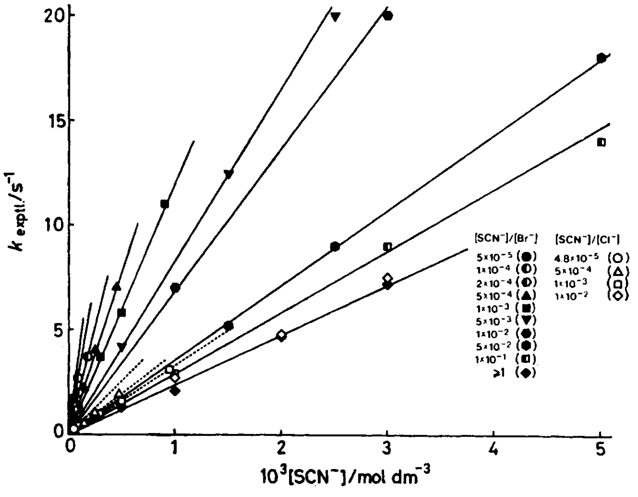
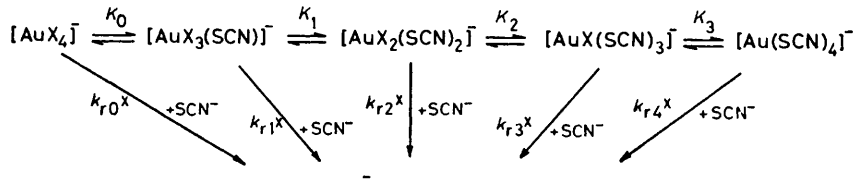


FIGURE 5 Plots of the observed rate constant for the reduction of Au^{III} by thiocyanate as a function of the thiocyanate concentration at constant [SCN$^-$]/[X$^-$]. X = Br (——) or Cl (- - -). The line with the lowest slope represents reduction of $[Au(SCN)_4]^-$



SCHEME 2 Stoicheiometric mechanism. K_n (n = 0—3) denote the stepwise equilibrium constants according to equation (4), $k_r{}^X$ (i = 0—4, X = Cl or Br) the reduction rate constants for the various complexes $[AuX_{4-i}(SCN)_i]^-$

Figure 5 shows plots of the experimental redox rate constants against the concentration of thiocyanate for the experiments in Table 3 with constant [SCN$^-$]/[X$^-$]. Obviously, the observed rate constants are proportional to the concentration of free thiocyanate for [SCN$^-$] ⩽ 5 mmol dm^{-3}, which supports the intermolecular mechanism, *i.e.* an attack on the complex by an outer-sphere thiocyanate. The stoicheiometric reaction mechanism in Scheme 2, where k_{ri}^X denotes reduction rate constants, can be used to describe the kinetics. In principle, each of the complexes $[AuX_{4-i}(SCN)_i]^-$ (i = 0—4) in rapid equilibrium with each other can be reduced by thiocyanate, so the overall rate can be written as in (17)

$$\mathrm{Rate} = \{\sum_{i=0}^{4} k_{ri}^X[AuX_{4-i}(SCN)_i^-]\}[SCN^-] \quad (17)$$

which gives the experimental first-order rate constant (18) for excess of thiocyanate. Equation (18) can be

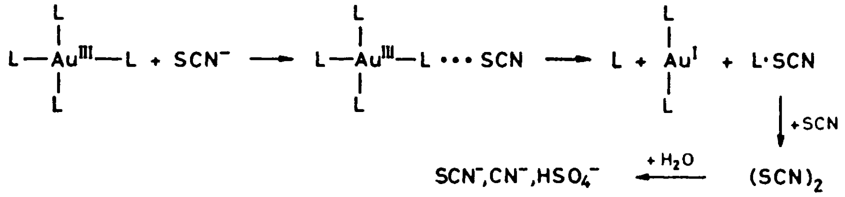
$$k_{\mathrm{exptl.}} = \frac{\sum_{i=0}^{4} k_{ri}^X \beta_i Q^i}{1 + \sum_{i=1}^{4} \beta_i Q^i} \times [SCN^-] \quad (18)$$

$$k_{\mathrm{exptl.}} = (\sum_{i=0}^{4} \alpha_i k_{ri}^X)[SCN^-] \quad (19)$$

$$\beta_{j+1} = \prod_{i=0}^{j} K_i,\ j = 0\text{—}3 \quad (20)$$

rearranged to (19), where Q = [SCN$^-$]/[X$^-$], β_i are stability constants defined by equation (20), and α_i denotes the fraction of gold present as $[AuX_{4-i}(SCN)_i]^-$.[11]

Thus, the observed redox rate constants are in principle sums of the constants k_{ri}^X (i = 0—4) for the parallel paths in Scheme 2, corrected for the distribution of the complexes present at each Q. Since the values of the equilibrium constants K_i are not known, the fractions α_i of equation (19) cannot be calculated, and the observed overall rate constants $k_{\mathrm{exptl.}}$ cannot be resolved into their components k_{ri}^X according to equation (19). Only k_{r4}^X for the reduction of $[Au(SCN)_4]^-$ can be determined as (2.4 ± 0.2) × 10^3 dm^3 mol^{-1} s^{-1} from the



(21)

plot in Figure 5 for the experiments with $[SCN^-]/[Cl^-] = 0.01$ and $[SCN^-]/[Br^-] \geqslant 1$, which have $\bar{n}_{SCN} = 4$. The value $k_{r0}^{Br} = (5 \pm 2) \times 10^4$ dm^3 mol^{-1} s^{-1} is obtained by extrapolation of $k_{exptl.}/[SCN^-]$ to small values of $[SCN^-]/[Br^-]$. Obviously, $[AuBr_4]^-$ is reduced faster than $[Au(SCN)_4]^-$. In the $[AuCl_4]^-$–thiocyanate system it is likely that only the complexes $[Au(SCN)_4]^-$ and $[AuCl(SCN)_3]^-$ contribute to the reduction, because of the large difference in stability between $[AuCl_4]^-$ and $[Au(SCN)_4]^-$.

Hall and Satchell[7] observed that the kinetics were chloride dependent. This is also compatible with the mechanism in Scheme 2. For instance, it follows directly from equation (19) that $k_{exptl.}$ will change with the concentration of halide for constant concentrations of thiocyanate, because this will change the distribution (α_i) of gold between the various complexes in the pre-equilibrium.

The experiments thus indicate an intermolecular mechanism for the redox process, *i.e.* a direct attack on a chloride, bromide, or thiocyanate ligand L of the complex by an outer-sphere thiocyanate in the rate-determining step according to (21). Subsequent reactions of L·SCN and $(SCN)_2$ are rapid.[16] This intimate mechanism is thus analogous to that used to describe square-planar $\longleftrightarrow$ octahedral redox reactions.[17-21] Intermolecular reduction has also been suggested for other gold(III) $\longleftrightarrow$ gold(I) redox processes.[9,22-24] The *ca.* twenty-fold difference in reduction rate between $[AuBr_4]^-$ and $[Au(SCN)_4]^-$ can be explained in terms of bromide being a better bridging ligand than thiocyanate.[25] The complexes ClSCN, BrSCN, and $(SCN)_2$ are sulphur bonded.[26] Thiocyanate is also co-ordinated to gold *via* the sulphur.[6] Therefore when thiocyanate is the bridging ligand, the electron transfer probably occurs *via* the sulphur atom.

The conclusions so far are valid for thiocyanate concentrations less than *ca.* 5 mmol dm^{-3}. It is obvious from the experiments shown in Figure 3 that for larger concentrations saturation occurs. This might be due to an accumulation of the intermediate (for L = SCN) in reaction (21). The redox kinetics in this interval of concentration will be the subject of further study.

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