Kinetics of the Monosubstitution of Chloride by Thiocyanate, Bromide, and Iodide in Tetrachloroaurate(III) Ions in Aqueous Solution: The Spectroscopic Detection of Reaction Intermediates, and Catalysis by Chloride Ions

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Kinetic and spectroscopic evidence is presented for the occurrence of intermediates in monosubstitution of $[AuCl_4]^-$ ions by thiocyanate and bromide ions in aqueous solution. The intermediate(s) is formed in a pre-equilibrium and then undergoes unimolecular decomposition to the products. The rates of both stages of the reaction have been studied using stopped-flow spectrophotometry; both stages exhibit a mild catalysis by added chloride ions. The monosubstitution of $[AuCl_4]^-$ by iodide ions displays no evidence for an intermediate but the overall reaction is again catalysed by chloride ions, here powerfully. Possible reaction mechanisms are discussed in the light of previous conclusions about the mechanisms of similar square-planar substitutions.

THERE exist a variety of kinetic studies of substitution in square-planar gold(III) complexes. The majority involve either the entry of amines into, or the displacement of amines from, chlorogold compounds. Most studies have used non-aqueous solvents, frequently methanol or acetone. Only a few systems have been examined using aqueous solutions, notably the chloride exchange[1] and the hydrolysis of tetrachloroaurate(III) ions, the latter reaction being perhaps the most frequently studied[2] of all the various substitutions. Discussions of the mechanism of substitution in gold(III) complexes, and in other square-planar complexes,[3] often involve postulates of five-co-ordinate intermediates, but such intermediates are rarely actually detected: the one really likely example involves substitution by an

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[1] R. L. Rich and H. Taube, *J. Phys. Chem.*, 1954, **58**, 1.

[2] See, for example, F. H. Fry, G. A. Hamilton, and J. Turkevich, *Inorg. Chem.*, 1966, **5**, 1943; P. van Z. Bekker and W. Robb, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 849; B. I. Peshchevitskii, V. I. Belantsev, and N. V. Kurbatova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1007; L. Carlsson and G. Lindgren, *Acta Chem. Scand.*, 1967, **21**, 819.

[3] See, for example, L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1145; C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.

amine in an elaborate rhodium complex.[4] Cattalini[5] concluded that conditions favourable for the detection of the five-co-ordinate intermediates are rarely likely to be met. We now report direct kinetic and spectroscopic evidence for the existence of intermediates during substitution by thiocyanate and bromide ions in tetrachloroaurate(III) ions in aqueous solution. Substitution by thiocyanate, and some other simple ions, has previously been investigated in methanol solution.[6]

EXPERIMENTAL

Materials.—Sodium tetrachloroaurate(III) was a previous sample.[7] All the other salts were samples of the purest available commercial materials.

Kinetic Arrangements.—(*a*) *Substitution by thiocyanate ions.* In aqueous solution the $[AuCl_4]^-$ ion has an absorption band at 312 nm (ε 4 200 dm^3 mol^{-1} cm^{-1}). In the presence of thiocyanate ions (which do not absorb in this region) there occurs a very rapid increase in absorption, centred at *ca.* 310 nm (ε 9 700 dm^3 mol^{-1} cm^{-1}), followed by a somewhat slower decrease in this absorption. At moderate acidities (where effectively all the thiocyanate exists as free $[SCN]^-$ ions) these absorption changes are too fast to measure by conventional procedures but can conveniently be monitored by the stopped-flow technique. The reactions were studied under pseudo-first-order conditions with thiocyanate ions in excess of the gold species. All the reaction mixtures contained sufficient chloride ions to repress the hydrolysis of the $[AuCl_4]^-$ ion[2] and sufficient perchloric acid to render negligible, in the times involved, the known autoreduction of gold(III) thiocyanate species.[8] It was possible to analyse separately the two parts of the evident stepwise process underlying the absorbance changes. Both the formation of the intermediate and its subsequent disappearance were first-order processes under the conditions used. A Durrum–Gibson stopped-flow spectrophotometer (path length, 2 cm), calibrated using a Unicam SP 800 recording spectrophotometer, was used for all the measurements. The temperature of the reaction mixtures could be controlled to within ±0.2 °C. The rate constants for the formation (k_1) and loss (k_2) of the intermediate were calculated from the oscilloscope traces either by measuring successive half-lives or by constructing first-order plots. Several traces were obtained for each set of reaction conditions and values of k_1 and k_2 were reproducible to within ±8%. The possible ambiguities in series-first-order processes discussed by Alcock *et al.*[9] do not apply to the present system in which it is possible to calculate the absorption coefficient of the intermediate directly. At 25°C the kinetic effects of changes in thiocyanate- and chloride-ion concentration, and in ionic strength, were examined (Table 1). Similar patterns of results were obtained at other temperatures.

TABLE 1

Reaction between thiocyanate and tetrachloroaurate(III) ions in aqueous solution at 25 °C. $[AuCl_4^-]_0 \simeq 4.0 \times 10^{-5}$ mol dm^{-3} (initial absorption at 312 nm, D_0 0.35); $[H_3O^+] = 0.002$ mol dm^{-3}; ionic strength (I) maintained with added $Na[ClO_4]$; for k_1, k_2, and D_I see text

(*i*) Effect of $[SCN^-]$ ($[Cl^-] = 0.10$ mol dm^{-3})

$10^2[SCN^-]$/mol dm^{-3}	k_1/s^{-1}		k_2/s^{-1}		D_I
	$I = 0.20$	1.00	$I = 0.20$	1.00	($I = 0.2$)
0.05	16.2		1.07		0.41
0.10	17.4	17.1	1.93	2.10	0.46
0.20	23.5	22.0	2.90	3.23	0.51
0.40	36.3	32.0	5.70	5.01	0.58
0.75	51.2		7.09		0.64
1.0	60.7	56.1	9.29	6.83	0.68
1.5	78.0	76.0	10.0	7.00	0.71
2.5	123		10.2		0.77
4.0	151		10.4		0.78

(*ii*) Effect of Cl^- ($I = 1.00$ mol dm^{-3})

$10[Cl^-]$/mol dm^{-3}	$10^2[SCN^-] = 0.20$ mol dm^{-3}		$10^2[SCN^-] = 1.5$ mol dm^{-3}	
	k_1/s^{-1}	k_2/s^{-1}	k_1/s^{-1}	k_2/s^{-1}
0.50	19.3	2.91	66.9	6.50
1.00	21.2	3.22	74.8	6.80
2.00	33.1	3.81	84.6	7.51
4.00	46.3	4.76		
6.00	57.7	5.54		
8.00	76.0	6.42		

TABLE 2

Reaction between bromide and tetrachloroaurate(III) ions in aqueous solution at 25 °C. $[AuCl_4]_0 \simeq 5.0 \times 10^{-5}$ mol dm^{-3} (initial absorption at 312 nm, D_0 0.42); $[H_3O^+] = 0.002$ mol dm^{-3}; $I = 0.20$ mol dm^{-3}; for k_1, k_2, and D_I see text

(*i*) Effect of $[Br^-]$ ($[Cl^-] = 0.10$ mol dm^{-3})

$10^2[Br^-]$/mol dm^{-3}	k_1/s^{-1}	k_2/s^{-1}	$D_I - D_0$
0.2	1.5	0.063	$\simeq 0.003$
0.5	2.6	0.13	
0.75	3.2	0.18	
1.00	3.8	0.25	$\simeq 0.016$
1.50	4.9	0.37	
2.00	7.7	0.48	$\simeq 0.025$
5.00	11	1.2	$\simeq 0.064$

(*ii*) Effect of $[Cl^-]$ ($I = 1.00$, $[Br^-] = 0.05$ mol dm^{-3})

$[Cl^-]$/mol dm^{-3}	k_1/s^{-1}	k_2/s^{-1}
0.05	9.7	1.1
0.10	11	1.2
0.40	14	1.4

(*b*) *Substitution by bromide ions.* The addition of an excess of bromide ions to an aqueous solution of $[AuCl_4]^-$ ions leads to generally similar absorption changes at 312 nm as does addition of thiocyanate ions: the absorption first increases (slightly) very rapidly and subsequently decreases somewhat more slowly to a value compatible with the absorption expected[10] for the species $[AuCl_3Br]^-$. These absorption changes are again sufficiently rapid to require the use of stopped-flow spectrophotometry. As for the thiocyanate system, the two phases of the reaction, the initial increase in absorption and the subsequent decrease, can be separated kinetically and the effects of changes in reaction conditions studied. Our general procedure followed that used for substitution by thiocyanate and the reproducibility of the observed first-order rate constants,

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[4] L. Cattalini, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, 1968, **90**, 4800.

[5] L. Cattalini, *Progr. Inorg. Chem.*, 1970, **13**, 263.

[6] L. Cattalini, A. Orio, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1967, **89**, 3130.

[7] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1976, 1278.

[8] J. Pouradier and M. C. Gadet, *J. Chim. phys.*, 1966, **63**, 1467.

[9] N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, 1970, **66**, 2210.

[10] J. Pouradier and M. Coquard, *J. Chim. phys.*, 1966, **63**, 1072; see also L. Almgren, *Acta Chem. Scand.*, 1971, **25**, 3713.

k_1 and k_2, was now within ±20 and ±10%, respectively (Table 2). At longer times further substitution by bromide [10] is evident but these processes were not studied in detail.

(*c*) *Substitution by iodide ions.* When iodide ions are mixed with $[AuCl_4]^-$ ions in aqueous solution there is, in contrast to the findings with bromide and thiocyanate ions, no transient increase in absorption at 312 nm, but only a decrease in absorption corresponding to the conversion of $[AuCl_4]^-$ into $[AuCl_3I]^-$. The spectra of the various possible chloroiodogold(III) complexes are unknown [owing to subsequent important reduction of gold(III) to gold(I) species when the I : Au ratio rises much above unity [7,11]], but absorbance measurements with solutions (*ca.* 10^{-4} mol dm^{-3}) containing various $[I^-] : [AuCl_4^-]$ ratios between 1.2 and 0.2 : 1 strongly suggest that the initial substitution of one chloride ion by iodide takes place quantitatively, and that $[AuCl_3I]^-$ does not absorb significantly at 312 nm. Relatively very little free iodine was detected over periods of up to 1 h for such conditions, but substantial reduction to Au^I was soon apparent at higher I : Au ratios and large increases in absorption then occurred owing to formation of the $[I_3]^-$ ion. Since the rate of reduction by iodide ions is not accurately known, we decided to study the kinetics of substitution under (second-order) conditions of equal concentrations of iodide and $[AuCl_4]^-$ ions where tests showed that negligible reduction occurs during the period of substitution. Our reaction conditions and results are in Table 3. In these iodide substitutions, since both reactants were always present in very low concentrations, the observed rates were sufficiently slow for reactions to be followed using a Unicam SP 800 instrument, the spectrophotometer cell serving as the reaction vessel. Reaction was initiated by the final addition of a small aliquot portion of a concentrated solution of potassium iodide. The second-order rate constants were calculated from plots of the standard equation $x/(a - x) = ak_{obs.}t$; $k_{obs.}$ was reproducible to within ±12%.

TABLE 3

Reaction between iodide and tetrachloroaurate(III) ions in aqueous solution at 25 °C. $[AuCl_4^-]_0 = [I^-]_0 = 10^{-4}$ mol dm^{-3}; $I = 2.50$ mol dm^{-3}; $[H_3O^+] = 0.002$ mol dm^{-3}; $k_{obs.}$ = observed second-order rate constant

$[Cl^-]$/mol dm^{-3}	0.1	0.2	0.4	0.6	0.8	1.0
$k_{obs.}$/dm^3 mol^{-1} s^{-1}	18.0	44.0	164	760	1 060	1 900

RESULTS AND DISCUSSION

Substitution by Thiocyanate Ions.—The observed absorbance changes discussed in the Experimental section clearly indicate the occurrence of an intermediate. The reaction occurs in two (approximately) separable steps, the rate of the first process (which leads to the increase in absorbance) being *ca.* 10 (or more) times that of the second (which leads to the decrease in absorbance) and being therefore approximately complete before a significant amount of the second step has taken place. The value of D_I in Table 1 is the maximum absorbance recorded during a given run. D_I itself reaches a maximum value ($D_I^{max.}$) at high thiocyanate concentrations and, for each set of conditions, reflects the concentration of intermediate (I) formed. Measurements over a range of wavelengths show that the intermediate has a bell-shaped absorption whose maximum is centred at *ca.* 310 nm. The values of D_I in Table 1 refer to 312 nm. Examination (Figure 1) of the various D_I values in Table 1 shows that they can be well represented by an equilibrium of the type (1), with a value of $K_1 = 320 \pm 30$ dm^3 mol^{-1} at 25 °C.

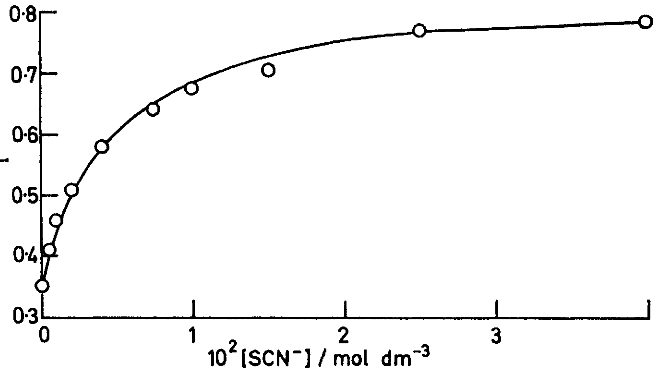

FIGURE 1 Plot of D_I against $[SCN^-]$ at $I = 0.20$ mol dm^{-3}. The continuous line represents values predicted using $D_0 = 0.35$, $D_I^{max.} = 0.80$, and $K_1 = 320$ dm^3 mol^{-1}

At the highest thiocyanate concentrations, effectively all the $[AuCl_4]^-$ ions are converted into (I) at equilibrium.

$$[AuCl_4]^- + [SCN]^- \overset{K_1}{\rightleftharpoons} [(I)]^{2-} \qquad (1)$$

The absorption coefficient of the intermediate can therefore be calculated from $D_I^{max.}$. An equilibrium such as (2), with n = 1—4, is not a satisfactory representation of the results since the concentration of (I) will be expected to be materially reduced by increases in the chloride-ion concentration. However, at fixed ionic strength, increases in $[Cl^-]$ at any value of $[SCN^-]$ have little effect on D_I, and lead, if anything, to a small increase. We suggest therefore that the observed first-order rate k_1 represents the rate of establishment of equilibrium (1) and hence, with $[SCN^-]_0 \gg [AuCl_4^-]_0$ and in the absence of other effects, $k_1 = k_1'[SCN^-]_0 + k_{-1}'$, where k_1' and k_{-1}' are the respective rate constants for the forward and reverse steps of equilibrium (1) and the subscript zero signifies initial concentration. Under such conditions the observed first-order constant k_2 refers to the loss of (I) to products. This step appears irreversible under our concentration conditions. We find that both k_1 and k_2 are increased somewhat by increases in $[Cl^-]$ at fixed ionic strength (Table 1). It is evident that the steps whose rates they reflect are catalysed by added chloride ions.

$$[AuCl_4]^- + n[SCN]^- \rightleftharpoons [(I)]^- + nCl^- \qquad (2)$$

The results as a whole can be satisfactorily represented by the scheme in (3), it being assumed for the sake of simplicity (and as the observed rates show to be a fair approximation) that the intermediates (I) and (II)

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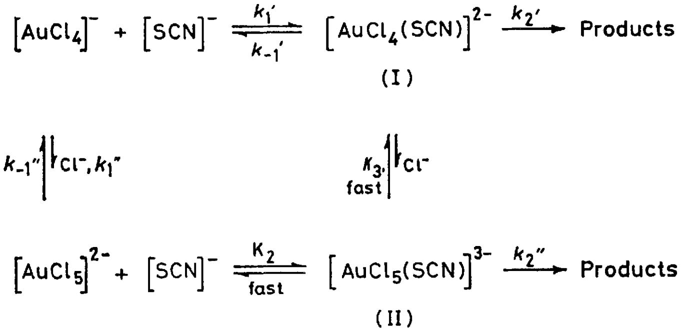
[11] A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, 1961, **35**, 2206.

are formed in rapid pre-equilibria. It is also assumed that $[(\mathrm{II})] \ll [(\mathrm{I})]$ at the chloride concentrations used. In (3) no particular assumptions are implied about the detailed structures of the intermediate gold species; these matters, and the nature of the products, are discussed below.



(3)

With $[\mathrm{SCN^-}]_0 \gg [\mathrm{AuCl_4^-}]_0$, as in all our reaction mixtures, it can be shown that (3) leads to equation (4) for the observed first-order rate constant (k_1) for approach to the pre-equilibrium. Equation (4) can be written as (5), in which $k_1''' = k_1''K_2$ and $k_{-1}''' = k_{-1}''K_3$.

$$k_1 = k_1'[\mathrm{SCN^-}]_0 + k_1''K_2[\mathrm{SCN^-}]_0[\mathrm{Cl^-}] + k_{-1}' + k_{-1}''K_3[\mathrm{Cl^-}] \tag{4}$$

$$k_1 = (k_1' + k_1'''[\mathrm{Cl^-}])[\mathrm{SCN^-}]_0 + (k_{-1}' + k_{-1}'''[\mathrm{Cl^-}]) \tag{5}$$

The observed first-order rate constant (k_2) for product formation is given, in the absence of significant catalysis by chloride ions, by equation (6) in which $K_1 = k_1'/k_{-1}'$ and, in the presence of mild catalysis, to a good approximation by equation (7) in which $k_2''' = k_2''K_3$.

$$k_2 = \frac{k_2'K_1[\mathrm{SCN^-}]_0}{(1 + K_1[\mathrm{SCN^-}]_0)} \tag{6}$$

$$k_2 = (k_2' + k_2'''[\mathrm{Cl^-}])\,\frac{K_1[\mathrm{SCN^-}]_0}{(1 + K_1[\mathrm{SCN^-}]_0)} \tag{7}$$

It is evident that, for any fixed value of $[\mathrm{Cl^-}]$, k_2 should reach a maximum value $k_2^{\mathrm{max.}} = (k_2' + k_2'''[\mathrm{Cl^-}])$ as $[\mathrm{SCN^-}]_0$ is increased. This is in agreement with experiment (Figure 2). Moreover, plots such as Figure 2 can be well reproduced using the experimental value of $k_2^{\mathrm{max.}}$ and a value of K_1 equal, within experimental error, to that obtained independently from the changes in absorbance (D_I) of the intermediate (see above). This self-consistency of the kinetic and absorbance results supports the analysis.

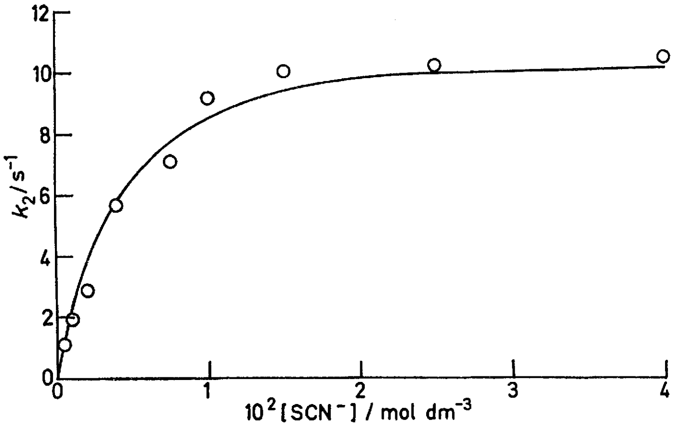


FIGURE 2 Plot of k_2 against $[\mathrm{SCN^-}]$ at $I = 0.20$ mol dm^{-3}, $[\mathrm{Cl^-}] = 0.10$ mol dm^{-3}, and $[\mathrm{H_3O^+}] = 0.002$ mol dm^{-3}. The continuous line represents values predicted using $k_2^{\mathrm{max.}} = 11.0$ s^{-1} and $K_1 = 350$ dm^3 mol^{-1}

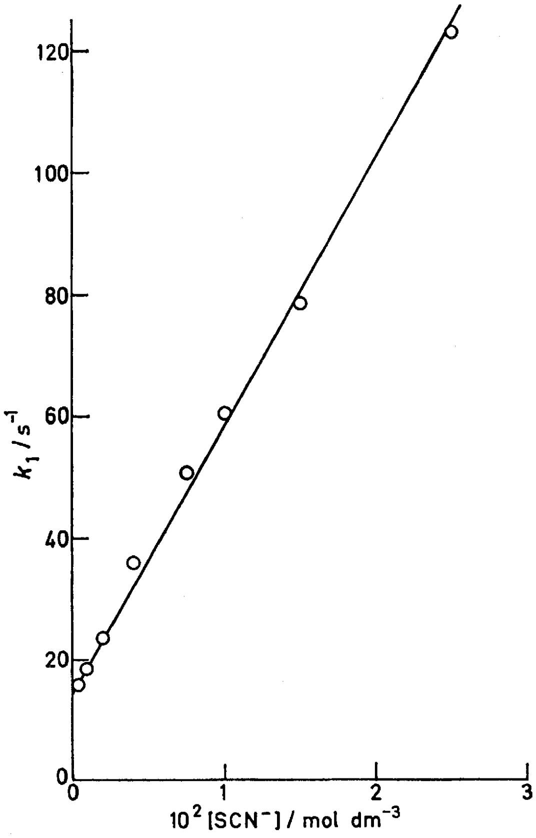


FIGURE 3 Plot of k_1 against $[\mathrm{SCN^-}]$ at $I = 0.20$ mol dm^{-3} (see Table 1)

Values for k_1', k_1''', k_{-1}', and k_{-1}''' can be obtained from the gradients and intercepts of plots (Figure 3) of k_1 against $[\mathrm{SCN^-}]_0$, at any fixed chloride concentration, using the fact that $k_1'/k_{-1}' = k_1'''/k_{-1}''' = K_1$. Values of these constants can also be obtained from plots of k_1 against [Cl$^-$], at any fixed thiocyanate concentration. The agreement is satisfactory (±20%) and our average values are in Table 4. Values for k_2' and k_2''' were obtained by plotting k_2 against [Cl$^-$] at any fixed value of [SCN$^-$]$_0$ (Figure 4). Self-consistent results were again obtained (±15%) (Table 4).

It seems clear that the observed processes consist of a rapid initial adduct formation between one thiocyanate and one [AuCl$_4$]$^-$ ion, followed by some unimolecular rearrangement or decomposition of this adduct. The possibility that the observed processes represent a rapid substitution of chloride by thiocyanate ions, followed by further substitution, or by (ligand) isomerisation of SCN, or by reduction of the gold(III) centre, is not easily compatible with (*i*) the clearly detected equilibrium process whose position is not materially affected by [Cl$^-$], and (*ii*) published reports of the rate of reduction in similar systems.[8] (The possible reductions of [AuBr$_4$]$^-$ ions by thiocyanate ions noted by Kazakov and Konovalova [12] are probably preceded by very rapid reactions of the type we report here.) It remains to consider (*a*) conceivable structures for (I), and (*b*) its mode of decomposition.

TABLE 4

Values of derived rate constants for the scheme in (3) at 25 °C. For definitions of rate constants see text

(*a*) I = 0.20 mol dm^{-3}

$k_1' = 3\,330$ dm^3 mol^{-1} s^{-1}, $k_{-1}' = 9.50$ s^{-1}, $k_1''' = 14\,000$ dm^6 mol^{-2} s^{-1}, $k_{-1}''' = 40$ dm^3 mol^{-1} s^{-1}, $(k_2' + 0.1\,k_2''') = 11.0$ s^{-1}

(*b*) I = 1.00 mol dm^{-3}

k_1', k_{-1}', k_1''' and k_{-1}''' have values within ±10% of those found at I = 0.20 mol dm^{-3}; $k_2' = 7.3$ s^{-1}, $k_2''' = 8.0$ dm^3 mol^{-1} s^{-1}

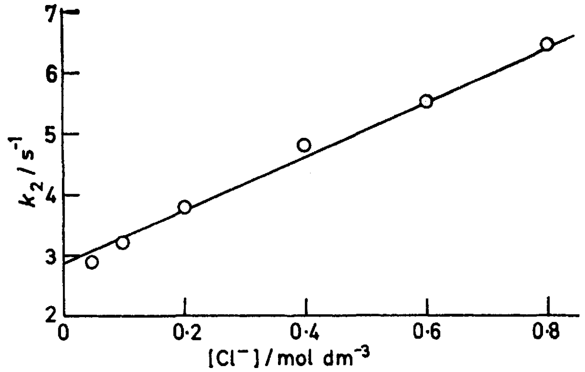
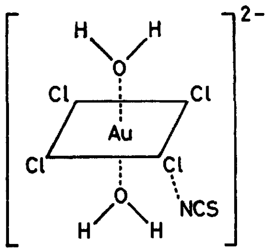


FIGURE 4 Plot of k_2 against [Cl$^-$] at 10^2[SCN$^-$] = 0.20 mol dm^{-3} and I = 1.00 mol dm^{-3}

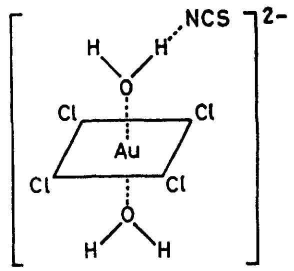
If (I) and, of course, (II) contain [SCN]$^-$ and [AuCl$_4$]$^-$ and, as we have argued, we are not concerned with ligand isomerism, then it is probable that the thiocyanate group is co-ordinated to the gold centre *via* the S atom. All the evidence points this way.[13] In the past at least three types of intermediate have been mooted for square-planar substitution: (*i*) some type of outer-sphere complex, here perhaps (III) or (IV); (*ii*) a square-pyramidal complex, *e.g.* (V); and (*iii*) a trigonal-bipyramidal complex, *e.g.* (VI). In the present context (III) and (IV) seem rather unlikely to possess sufficient stability or to lead to the observed increase in absorbance. Although both (V) and (VI) could conceivably lead to an increased absorbance compared with [AuCl$_4$]$^-$, species like (V) are normally[3] regarded as more stable than species like (VI). We conclude therefore that the intermediate (I) is most probably (V), whose subsequent decomposition [equation (8)], *via* a transition state similar to (VI), leads to the observed decrease in absorbance. For intermediate (II) the likely structure is the

$$\text{(V)} \xrightarrow{k_2'} \text{Cl}^- + [\text{AuCl}_3(\text{SCN})]^- \qquad (8)$$

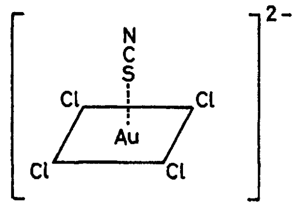
(loose) octahedral form (VII). For the scheme in (3) to be valid it has to be assumed that (VII) decomposes more rapidly than does (V) to a form in which SCN has entered the square plane (*i.e.* $k_2'' > k_2'$). This assumption is supported by the results obtained for substitution by iodide ions. Catalysis of reactions of [AuCl$_4$]$^-$ ions by chloride ions has also recently been reported in other contexts.[14] The probably[3] large charge separations in species (V) and (VII) may underlie the small effects of ionic strength in these reactions, especially since, in the range studied, these effects are, in any event, likely to be slight.



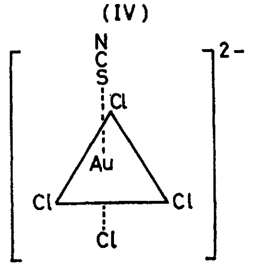
(III)



(IV)



(V)



(VI)

Substitution by Bromide Ions.—Fewer measurements were made with this system (Table 2) because the initial increase in absorbance is much smaller and cannot easily be measured accurately. The general pattern of

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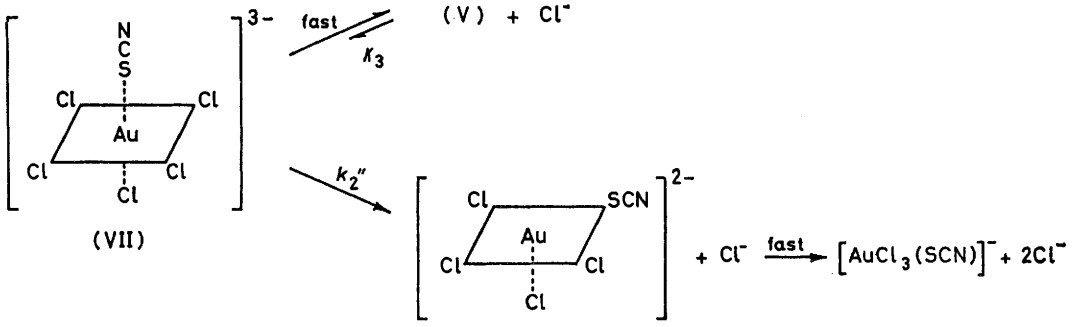
[12] V. P. Kazakov and M. V. Konovalova, *Russ. J. Inorg. Chem.*, 1968, **13**, 447.

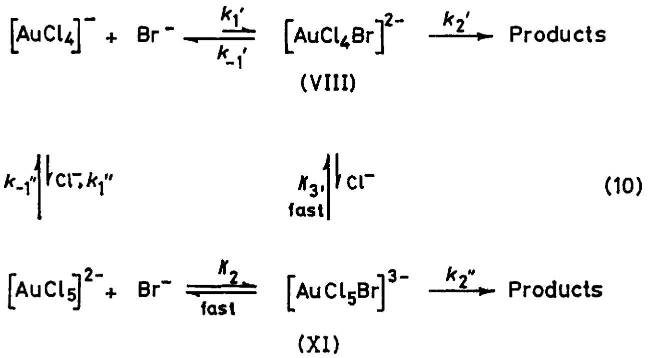
[13] A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.

[14] G. Annabile, L. Cattalini, A. A. El-Awady, and G. Natile, *J.C.S. Dalton*, 1974, 802; A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 1351.



(VII)

(9)



(VIII)

(XI)

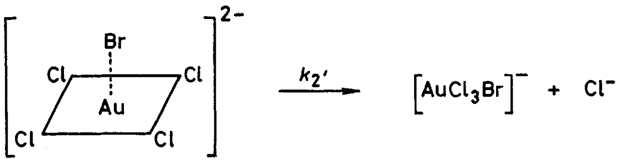
(10)

observations is, however, similar to that for the thiocyanate reaction: there is an initial very rapid reaction, leading to the small increase in absorbance, followed by a somewhat slower process, during which the absorption decreases. The two phases of the overall process are (approximately) separable, the second step being *ca.* 10-times slower than the first. Although measurement of the absolute magnitude of the initial increase in absorbance is difficult, oscillograph scale expansion permits the rate constant of the first step (k_1) to be measured to within ±20%; k_2 can be obtained more accurately (±10%) since an appreciable decrease in absorbance accompanies the second step. A small but detectable catalysis of both steps by chloride ions is again observed. The results suggest that the bromide system [scheme in (10)] differs from the thiocyanate system principally in the position of the pre-equilibrium, which now lies to the left. This conclusion follows from the (tentative) D_{I} values and from the fact that k_2 is

$$k_2 = (k_2' + k_2'''[\text{Cl}^-])\frac{K_1[\text{Br}^-]_0}{(1 + K_1[\text{Br}^-]_0)} \qquad (11)$$

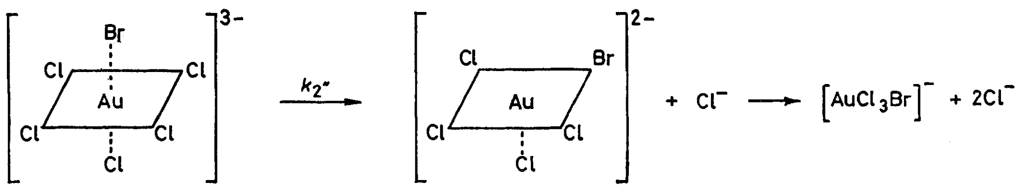
now proportional to $[\text{Br}^-]$ for all the values of $[\text{Br}^-]$ used.

For scheme (10) the equation analogous to (7) is (11). If $K_1[\text{Br}^-] \ll 1$ at all the values of $[\text{Br}^-]$, then $k_2 \simeq K_1[\text{Br}^-](k_2' + k_2'''[\text{Cl}^-]) = k[\text{Br}^-]$, at any fixed value of $[\text{Cl}^-]$, as found experimentally. It is assumed that self-catalysis by bromide ions (*via* $[\text{AuCl}_4\text{Br}]^{3-}$) is negligible compared with that by chloride ions. This is reasonable in view of the concentrations ranges used and the relatively slight catalysis by chloride ions (Table 2).



(VIII)

(12)



(IX)

(13)

The important aspect of the results with bromide ions is their general similarity to those obtained with thiocyanate ions for, with bromide, ambiguities arising from the possibility of ligand isomerism or of rapid reduction to gold(I) species are largely removed.* It seems

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* We have recently also detected five-co-ordinate intermediates in the substitution of thioamides into $[\text{AuCl}_4]^-$ ions.[15]

[15] A. J. Hall and D. P. N. Satchell, *Chem. and Ind.*, 1976, 373.

sensible too that K_1 should be smaller for bromide than for thiocyanate. The k_1 and k_2 values, obtained under similar conditions of concentration, are 20—30 times smaller for the bromide than for the thiocyanate substitution. This finding is compatible with results obtained using methanol solutions.[6]

Intermediates (VIII) and (IX) probably have structures analogous to those postulated for the thiocyanate system and decompose to $[AuCl_3Br]^-$ [whose (approximate) absorption at 312 nm is known from previous work [10]].

Substitution by Iodide Ions.—Here, owing to concomitant reduction, it was possible only to study the reaction under second-order conditions (see Experimental section). The observed reaction is (14). Our results are in Table 3. No intermediate was detected in this

$$[AuCl_4]^- + I^- \xrightarrow{k_{obs.}} [AuCl_3I]^- + Cl^- \qquad (14)$$

reaction, possibly owing to its very low concentration and/or to its having an absorbance smaller than that of $[AuCl_4]^-$ at the measured wavelength. The important aspect of the results in Table 3 is the evident catalysis of substitution by chloride ions. The observed rate equation has the approximate form (Figure 5) Rate = $k[AuCl_4^-][I^-][Cl^-]^2 = k_{obs.}[AuCl_4^-][I^-]$. The uncatalysed rate appears to be small compared with the catalysed rate ($[Cl^-]$ cannot be reduced too far for otherwise significant hydrolysis of the $[AuCl_4]^-$ ions occurs [2]). A mechanism such as (15) is presumably involved. Why substitution by iodide ions into a position on the square plane should be so much faster *via* six-co-ordinate than five-co-ordinate species formed from I^- and $[AuCl_4]^-$ alone is not obvious, but the phenomenon qualitatively supports the assumption made concerning the relative reactivities of five- and six-co-ordinate species in the thiocyanate and the bromide reactions. The apparent common occurrence of catalysis by chloride ions in the reactions of chlorogold(III) species suggested by our work may have important implications for square-planar substitution generally. This type of effect has been rarely examined deliberately.

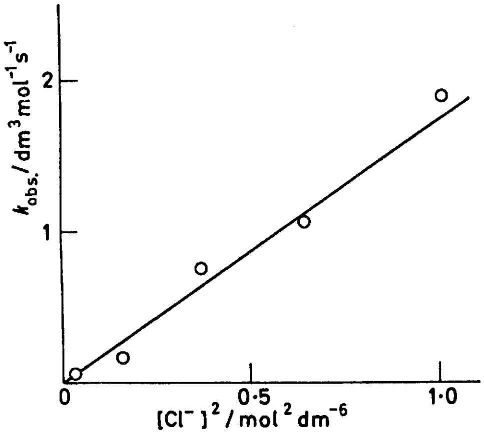
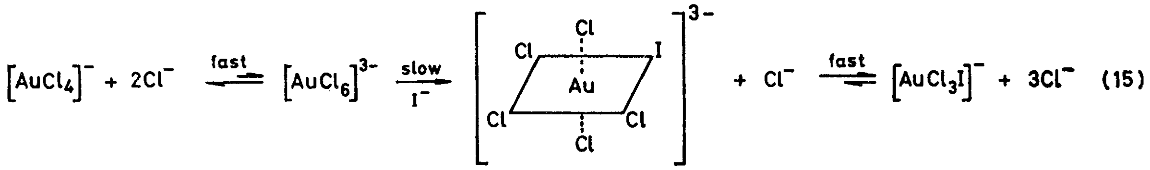


FIGURE 5 Chloride-ion catalysis of substitution by iodide ions



(15)

[6/2256 *Received*, 13*th December*, 1976]