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Kinetics, Mechanism and Equilibria for Halide Substitution Processes of Chloro Bromo Complexes of Gold(III)

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The over-all process

$$AuCl_4^- + 4Br^- \rightarrow AuBr_4^- + 4Cl^-$$

has been studied at 25.0 °C in a 1.00 M sodium perchlorate medium using stopped-flow spectrophotometry. The stoichiometric mechanism for the reaction has been derived and the twelve rate constants have been determined. The stepwise substitutions take place *via* direct halide displacements, the solvent path being negligible. The kinetics give no evidence for slow formation of long-lived intermediate five-coordinated associates between the square-planar complex and the entering halide, which has been suggested in recent literature.

The kinetic behaviour of analogous platinum(II) and gold(III) complexes is compared. *cis*- and *trans*-effects are of the same order of magnitude, but the nature of the entering group is much more important for the reactions of the gold complexes. The ratio in reactivity Au(III)/Pt(II) is *ca.* 2 × 10^6 for bromide, 10^5 for chloride and only 10^3 for water as the entering group.

The equilibrium constants,

$$K_n = \frac{[AuCl_{4-n}Br_n^-][Br^-]}{[AuCl_{3-n}Br_{n+1}^-][Cl^-]}$$

determined from kinetics, are 240 ± 40, 98 ± 20, 49 ± 10, and 17 ± 5 for $n = 0, 1, 2$ and 3, respectively. These constants give $\lg(\beta_{4Br}/\beta_{4Cl}) = 7.3 \pm 0.3$ for the over-all stability constants β_{4X} for the halide complexes AuX_4^- (X = Cl,Br). Charge-transfer spectra for the complexes $AuCl_{4-n}Br_n^-$ ($n = 0, 1, 2, 3, 4$) have been obtained and spectral assignments are proposed.

The kinetics for the reaction between $AuCl_4^-$ and bromide have been studied earlier in methanol[1] and in aqueous solution[2,3] giving discordant results. For instance, Louw and Robb[2] observed only one single reaction step for the over-all process (1),

$$AuCl_4^- + 4Br^- \rightleftharpoons AuBr_4^- + 4Cl^- \quad (1)$$

which was interpreted to be a rate-determining replacement of the first chloride by bromide. The other two studies[1,3] report two-stage reactions, however. Cattalini *et al.*[1] interpreted these two steps as two consecutive ligand substitutions, whereas Hall and Satchell,[3] in their recent paper, concluded that the first step is the formation of a five-coordinate intermediate complex between $AuCl_4^-$ and bromide, and the second one a formation of $AuCl_3Br^-$ from this intermediate, subsequent substitutions of chloride being assumed to be much slower. The proposed solvent paths[1,2] (the k_1-term in the usual square-planar substitution rate law[4]) are also questionable, since the interpretation of intercepts in the kinetic plots depends on the kinetic model used.

A detailed study of the $AuCl_4^-$-bromide reaction was thus desirable, and this would also enable a comparison of the kinetic behaviour of the gold(III) chloro bromo complexes and the analogous platinum(II) complexes, which have recently been studied.[5]

The present investigation shows that the stepwise substitution reactions (2)

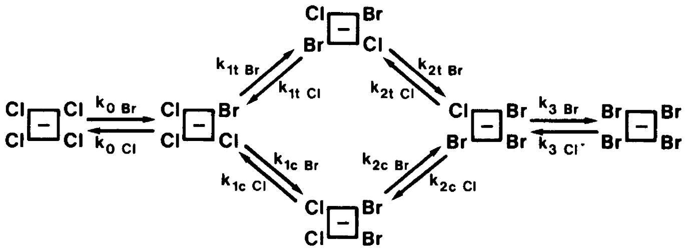


Fig. 1. Stoichiometric model for reaction (1).

$$AuCl_{4-n}Br_n^- + Br^- \underset{k_{nCl}}{\overset{k_{nBr}}{\rightleftharpoons}} AuCl_{3-n}Br_{n+1}^- + Cl^- \qquad (2)$$

take place *via* the stoichiometric mechanism in Fig. 1. We have previously used that model for the $PtCl_4^{2-}$-bromide reaction.[5] The halide substitution rate constants defined in the figure are related to the equilibrium constants K_n, $n=0, 1, 2, 3$ by eqn. (3):

$$K_n = k_{nBr}/k_{nCl} = \frac{[AuCl_{3-n}Br_{n+1}^-]}{[AuCl_{4-n}Br_n^-]} \times \frac{[Cl^-]}{[Br^-]} \qquad (3)$$

$AuCl_2Br_2^-$ appears as *cis*- and *trans*-isomers, denoted by the subscripts c and t in the following text.

The following reactions have been studied using stopped-flow spectrophotometry:

$$AuCl_4^- + Br^- \underset{k_{0Cl}}{\overset{k_{0Br}}{\rightleftharpoons}} AuCl_3Br^- + Cl^- \qquad (4)$$

$$AuClBr_3^- + Br^- \underset{k_{3Cl}}{\overset{k_{3Br}}{\rightleftharpoons}} AuBr_4^- + Cl^- \qquad (5)$$

$$AuCl_3Br^- + Br^- \xrightarrow{k_{1tBr}} trans\text{-}AuCl_2Br_2^- + Cl^- \qquad (6)$$

$$trans\text{-}AuCl_2Br_2^- + Br^- \xrightarrow{k_{2tBr}} AuClBr_3^- + Cl^- \qquad (7)$$

$$cis\text{-}AuCl_2Br_2^- + Br^- \xrightarrow{k_{2cBr}} AuClBr_3^- + Cl^- \qquad (8)$$

Equilibrium constants K_n and spectra for the complexes $AuCl_{4-n}Br_n^-$, $n=0, 1, 2, 3, 4$, have also been determined.

EXPERIMENTAL

Chemicals. Hydrogen tetrachloroaurate(III) trihydrate, $HAuCl_4.3H_2O$ (Mallinckrodt or Degussa) was used directly. Anal. Calc.: Au 50.0; Cl 35.5.

Table 1. Reaction (4) followed in the forward and reverse directions. Wavelength 327 nm. $C_{Au}=1.0 \times 10^{-5}$ M. $[H^+]=2$ mM or 20 mM. Ionic strength 1.00 M.

$10^3[Cl^-]$/M	$10^3[Br^-]$/M	k_{exp}/s^{-1}
$AuCl_4^- + Br^- \rightleftharpoons AuCl_3Br^- + Cl^-$		
300	0.3	0.108 ± 0.05
300	0.5	0.120 ± 0.06
300	0.6	0.128 ± 0.007
300	0.8	0.140 ± 0.007
300	1.0	0.153 ± 0.008
500	0.5	0.183 ± 0.009
500	1.0	0.212 ± 0.010
500	1.2	0.233 ± 0.010
500	1.5	0.249 ± 0.012
500	1.7	0.264 ± 0.013
800	0.5	0.249 ± 0.012
800	1.0	0.287 ± 0.014
800	2.0	0.333 ± 0.017
800	3.0	0.396 ± 0.018
$AuCl_3Br^- + Cl^- \rightleftharpoons AuCl_4^- + Br^-$		
250	0.15	0.078 ± 0.005
350	0.15	0.102 ± 0.005
450	0.15	0.135 ± 0.007
550	0.15	0.161 ± 0.008
250	0.10	0.077 ± 0.005
350	0.10	0.099 ± 0.005
450	0.10	0.130 ± 0.006
550	0.10	0.155 ± 0.008
250	0.05	0.072 ± 0.005
350	0.05	0.101 ± 0.005
450	0.05	0.132 ± 0.006
550	0.05	0.160 ± 0.008

Table 2. Reaction (5) followed in the forward and reverse directions. Wavelength 400 nm. $[H^+]=20$ mM. C_{Au} was 2.0×10^{-4} or 1.0×10^{-4} M.

$10^3[Br^-]$/M	$10^3[Cl^-]$/M	k_{exp}/s^{-1}
$AuClBr_3^- + Br^- \rightleftarrows AuBr_4^- + Cl^-$		
250	79	47±3
250	74	50±3
250	69	41±2
250	64	41±2
250	59	42±2
350	450	59±3
350	250	70±4
350	79	59±3
350	74	58±3
350	69	59±3
350	64	64±3
350	59	61±3
450	450	84±3
450	250	83±3
450	79	82±3
450	74	79±3
450	69	78±4
450	64	70±3
450	59	83±3
550	450	101±5
550	250	99±4
550	79	99±4
550	74	93±4
550	69	96±5
550	64	100±5
550	59	103±5
$AuBr_4^- + Cl^- \rightleftarrows AuClBr_3^- + Br^-$		
350	200	64.0±0.7
350	300	65.3±0.8
350	400	66.3±0.7
350	500	67.7±0.7
250	200	48.4±0.5
250	300	49.7±0.5
250	400	50.5±0.5
250	500	51.8±0.8
75	100	14.5±0.4
75	200	16.5±0.5
75	300	17.0±0.5
75	400	18.0±0.7
75	500	19.0±0.6

Found: Au(grav.) 49.9±0.3, Cl (Mohr titr.) 35.5±0.2. 1.00 M stock solutions were prepared from perchloric acid (Baker's *p.a.*), sodium perchlorate (Baker's *p.a.*), sodium chloride (Merck's *p.a.*), sodium bromide (Merck's *p.a.*) and water, doubly distilled from quartz vessels.

Kinetics. The reactions were followed at 25.00 ±0.02 °C using a modified Durrum-Gibson stopped-flow instrument. The metal solution (M) contained the gold complex and sometimes also chloride and/or bromide to adjust the mean ligand number at the start of the experiment. The ligand solution (L) contained chloride and/or bromide. Tables 1 to 3 give the concentrations after mixing, all solutions having the ionic strength 1.00 M, with sodium perchlorate as the supporting electrolyte. The hydrogen ion concentration was varied within the interval $2\ \text{mM} \leq [H^+] \leq 0.5$ M by substitution of part of the sodium perchlorate of the M-solution by perchloric acid. This variation had no influence on the reaction rates. The equilibrium constant for reaction (9)

$$AuCl_4^- + H_2O \rightleftharpoons AuCl_3OH^- + Cl^- + H^+ \qquad (9)$$

has been determined to 2.4×10^{-6} M^2 [6,7] or 7×10^{-7} M^2,[8] and for the corresponding bromo complex to 3×10^{-8} M^2,[2] or 3×10^{-9} M^2,[8] so the hydrogen and halide ion concentrations used were sufficiently large to suppress the formation of hydroxo complexes in all experiments.

Large excess of chloride and bromide compared to gold gave pseudo first-order kinetics. Rate constants were calculated from first-order rate expressions using a least-squares programme and a computer.

The equilibrium reaction (4) was followed from both directions, see Table 1. In one series of experiments, solution M contained 2×10^{-5} M $AuCl_4^-$ and 0.60 M, 0.80 M or 1.00 M NaCl and solution L NaBr (0.6 to 6 mM) and – for $[Cl^-]=0.800$ M – NaCl (0.800 M) also. The reaction product in these runs was mainly $AuCl_3Br^-$; *cf.* Fig. 8. In another series, the gold solution M contained an equilibrium mixture of $AuCl_4^-$ and $AuCl_3Br^-$ (C_{Au} was 2×10^{-5} M, C_{Cl} 0.100 M and C_{Br} 0.300, 0.200 or 0.100 mM; *cf.* Fig. 8), and solution L contained sodium chloride (0.40, 0.60, 0.80 or 1.00 M).

Reaction (5) – see Table 2 – was started either by adding excess bromide ($C_{Br}=0.400$, 0.600, 0.800 or 1.000 M) to an equilibrated gold solution containing mainly $AuClBr_3^-$ and $AuBr_4^-$ (C_{Au} was 2×10^{-4} or 4×10^{-4} M, and C_{Cl} was 0.900, 0.500, 0.158, 0.148, 0.138, 0.128, or 0.118 M; *cf.* Fig. 8), or by adding sodium chloride ($C_{Cl}=0.200$, 0.400, 0.600, 0.800 or 1.000 M) to a solution of $AuBr_4^-$ ($C_{Au}=2\times10^{-4}$ M, C_{Br} was 0.150, 0.500 or 0.700 M) to give a mixture of $AuBr_4^-$ and $AuClBr_3^-$ at equilibrium. Large concentrations of chloride are required, which limits the possibilities to vary the ratio $[Cl^-]/[Br^-]$.

Reaction (6) – see Table 3 – was followed by mixing an M-solution having $C_{Au}=2\times10^{-5}$ M,

Table 3. Reactions (6), (7) and (8). Wavelengths 365 nm (6), 332 or 365 nm (7) 365 nm (8).

$10^3[Br^-]$/M	$10^3[Cl^-]$/M	10^5C_{Au}/M	$[H^+]$/M	k_{exp}/s^{-1}
$AuCl_3Br^- + Br^- \rightarrow$ *trans*-$AuCl_2Br_2^- + Cl^-$				
100	100	1.0	0.100	23 ± 2
150	100	1.0	0.100	34 ± 3
200	100	1.0	0.100	52 ± 4
300	100	1.0	0.100	69 ± 8
400	100	1.0	0.100	93 ± 9
500	100	1.0	0.100	120 ± 11
trans-$AuCl_2Br_2^- + Br^- \rightarrow AuClBr_3^- + Cl^-$				
200	–	2.5	0.500	5.6 ± 0.8
300	–	2.5	0.500	9.3 ± 0.4
400	–	2.5	0.500	11.8 ± 0.5
500	–	2.5	0.500	15.5 ± 0.9
201	50	5.0	0.020	6.1 ± 0.3
301	50	5.0	0.020	8.8 ± 0.3
401	50	5.0	0.020	11.7 ± 0.4
501	50	5.0	0.020	15.6 ± 0.5
cis-$AuCl_2Br_2^- + Br^- \rightarrow AuClBr_3^- + Cl^-$				
200	50	5.0	0.020	90 ± 20
300	50	5.0	0.020	134 ± 20
400	50	5.0	0.020	177 ± 20
500	50	5.0	0.020	230 ± 30

$C_{Cl} = 0.200$ M, C_{Br} 0.30 mM, 0.50 mM or 0.80 mM, and $C_{H^+} = 0.200$ M with L-solutions of sodium bromide (0.200, 0.300, 0.400, 0.600, 0.800 or 1.000 M). At the start of the kinetics, gold is present mainly as $AuCl_3Br^-$ and $AuCl_4^-$; see Fig. 8. Reaction (6) can be observed as a fast initial process followed by the much slower reaction between $AuCl_4^-$ and bromide; *cf.* the rate constants in Fig. 7.

Reaction (7) – see Table 3 – was started by mixing an L-solution of sodium bromide (0.400, 0.300, 0.800 or 1.00 M) with an M-solution containing 5×10^{-5} M $AuCl_3H_2O^-$ in 1.00 M $HClO_4$. The latter was prepared immediately before use in the kinetic studies by slow addition at 25 °C of 10 ml of 25.0 mM $AgNO_3$ (Merck's *p.a.*) to 10 ml 25.0 mM $HAuCl_4$ dissolved in 1.00 M perchloric acid, and subsequent separation of the silver chloride precipitate. After mixing, the following reactions take place:

$$AuCl_3H_2O \xrightarrow[\text{fast}]{+Br^-} AuCl_3Br^- \xrightarrow[\text{fast}]{+Br^-} trans\text{-}AuCl_2Br_2^- \xrightarrow[\text{slow}]{+Br^-} AuClBr_3^-$$

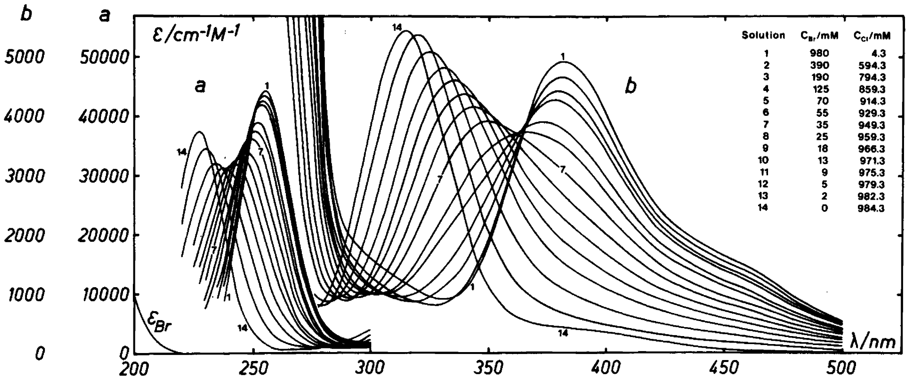
The two fast reactions are complete within less than one half-life of the slow process. The subsequent reaction $AuClBr_3^- \rightarrow AuBr_4^-$ is fast (*cf.* Fig. 7). Table 3 also contains the results of some experiments on reaction (7) performed by mixing L-solutions of sodium bromide (0.400, 0.600, 0.800 or 1.000 M) with an M-solution, having $C_{Au} = 1 \times 10^{-4}$ M, $C_{Cl} = 0.100$ M, $C_{Br} = 1.60$ mM and $C_{H^+} = 0.040$ M. This solution contains mainly the complexes $AuCl_3Br^-$, $AuCl_2Br_2^-$ and $AuClBr_3^-$; *cf.* Fig. 8. After mixing, the following reactions take place

$$AuCl_3Br^- \xrightarrow[\text{fast}]{+Br^-} trans\text{-}AuCl_2Br_2^- \xrightarrow[\text{slow}]{+Br^-} AuClBr_3^- \xrightarrow[\text{fast}]{+Br^-} AuBr_4^-$$

$$cis\text{-}AuCl_2Br_2^- \xrightarrow[\text{fast}]{+Br^-} AuClBr_3^- \xrightarrow[\text{fast}]{+Br^-} AuBr_4^-$$

The fast reactions are complete within less than one half-life of the slow process (7).

Reaction (8) was started by mixing an M-solution, having $C_{Au} = 1 \times 10^{-4}$ M, $C_{Cl} = 0.100$ M, $C_{Br} = 2$ mM



Solution	C_{Br}/mM	C_{Cl}/mM
1	980	4.3
2	390	594.3
3	190	794.3
4	125	859.3
5	70	914.3
6	55	929.3
7	35	949.3
8	25	959.3
9	18	966.3
10	13	971.3
11	9	975.3
12	5	979.3
13	2	982.3
14	0	984.3

Fig. 2. Molar absorptivities, $\varepsilon = e/C_{Au}$, where e denotes absorptivity for equilibrated solutions with different ratios C_{Br}/C_{Cl}. C_{Au} was 0.171 mM. Curve 14 represents 100 % $AuCl_4^-$, curve 1 100 % $AuBr_4^-$.

and $C_{H^+} = 0.040$ M with L-solutions of sodium bromide ($C_{Br} = 0.400$, 0.600, 0.800 or 1.00 M). The equilibrated M-solution contains mainly the complexes $AuCl_2Br_2^-$, $AuClBr_3^-$ and $AuBr_4^-$, so the following reactions take place after mixing:

$$trans\text{-}AuCl_2Br_2^- \xrightarrow[\text{slow}]{+Br^-} AuClBr_3^- \xrightarrow{+Br^-} AuBr_4^-$$

$$cis\text{-}AuCl_2Br_2^- \xrightarrow[\text{fast}]{+Br^-} AuClBr_3^- \xrightarrow{+Br^-} AuBr_4^-$$

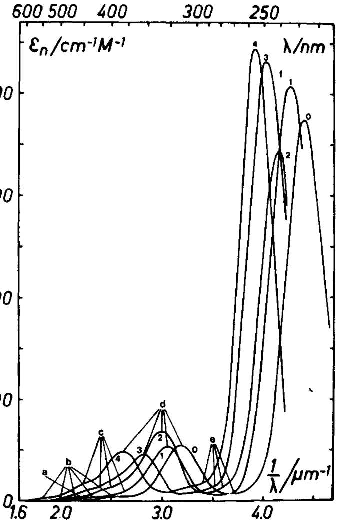


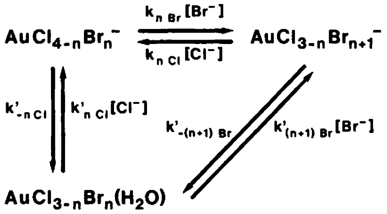
Fig. 3. Molar absorptivities, ε_n, for the complexes $AuCl_{4-n}Br_n^-$, $n = 0$, 1, 2, 3, 4, calculated from the curves in Fig. 2. and the equilibrium constants in Table 5. Assignments, see Table 7.

The reaction of the *cis*-isomer is about fifteen times faster than that of the *trans*-isomer, so these two reactions are kinetically separated. The subsequent reaction $AuClBr_3^- \rightarrow AuBr_4^-$ is only about 4 times slower than the $cis\text{-}AuCl_2Br_2^- \rightarrow AuClBr_3^-$ reaction, but reaction (8) can be followed at 365 nm, where $AuClBr_3^-$ and $AuBr_4^-$ have equal molar absorptivities (*cf.* Fig. 3).

Spectra. Fig. 2 shows spectra of a series of equilibrated solutions recorded using a Cary 15 Recording Instrument. The resolved spectra of the complexes shown in Fig. 3 were calculated using these curves and the equilibrium constants in Table 5.

RESULTS AND DISCUSSION

Rate expressions. The halide substitutions (4) to (8) can be described by the scheme (10) (*cf.* Refs. 4, 9) with $n = 0$, 1, 2, 3 and with *cis*- and *trans*-isomers for $n = 1$, 2:



(10)

For excess halide and with steady-state conditions for the intermediate aqua complex the pseudo first-order rate constant is described by eqn. (11). (Integration of rate law for reversible processes, *cf.* Ref. 10).

$$k_{\exp} = k_{n\mathrm{Cl}}[\mathrm{Cl}^-] + k_{n\mathrm{Br}}[\mathrm{Br}^-] + k'_{-n\mathrm{Cl}} \times \left(1 + \frac{k_{n\mathrm{Cl}}[\mathrm{Cl}^-]}{k_{n\mathrm{Br}}[\mathrm{Br}^-]}\right) \Bigg/ \left(1 + \frac{k'_{-n\mathrm{Cl}}}{k'_{-(n+1)\mathrm{Br}}} \times \frac{k_{n\mathrm{Cl}}[\mathrm{Cl}^-]}{k_{n\mathrm{Br}}[\mathrm{Br}^-]}\right) \quad (11)$$

Reaction (4) ($n=0$) was studied using such chloride and bromide concentrations that the predominant complexes at equilibrium were $\mathrm{AuCl_4^-}$ or $\mathrm{AuCl_4^-}$ and $\mathrm{AuCl_3Br^-}$, *cf.* Table 1. The rate constant $k'_{-0\mathrm{Cl}}$ for the acid hydrolysis of $\mathrm{AuCl_4^-}$ is about 0.02 $\mathrm{s^{-1}}$.[11,12] The rate constant $k'_{-1\mathrm{Br}}$ for acid hydrolysis of the bromide in $\mathrm{AuCl_3Br^-}$ is then approximately 0.02/4 $\mathrm{s^{-1}}$, since the leaving ligand effect is negligible (compare rate constants for the corresponding platinum complexes in Ref. 5, Table VIII). The third term in eqn. (11) therefore never amounts to more than about 0.006 $\mathrm{s^{-1}}$, which is much less than the observed rate constants. Thus, the reaction *via* the aqua complex can be neglected for the experimental conditions used, and eqn. (11) is simplified to (12):

$$k_{\exp} = k_{n\mathrm{Cl}}[\mathrm{Cl}^-] + k_{n\mathrm{Br}}[\mathrm{Br}^-] \quad (12)$$

Similarly, for reaction (5), ($n=3$) the chloride and bromide concentrations were chosen to give $\mathrm{AuClBr_3^-}$ and $\mathrm{AuBr_4^-}$ or $\mathrm{AuBr_4^-}$ predominantly at equilibrium. The acid hydrolysis rate constant for $\mathrm{AuBr_4^-}$, $k'_{-4\mathrm{Br}}$, is 0.2 $\mathrm{s^{-1}}$,[2] so the rate constant for hydrolysis of the chloride in $\mathrm{AuClBr_3^-}$, $k'_{-3\mathrm{Cl}}$, is approximately 0.2/4 $\mathrm{s^{-1}}$. In this case, the third term in eqn. (11) is always smaller than about 0.20 $\mathrm{s^{-1}}$, which is also negligible compared to the experimental rate constants. Thus, eqn. (12) is applicable for reaction (5) as well.

For reactions (6) to (8) ($n=1, 2$) all acid hydrolysis rate constants involved are much smaller than the observed rate constants which means that the reactions *via* aqua complexes can also be neglected in these cases. Furthermore, the reverse reactions are suppressed for the halide concentrations used, so eqn. (12) reduces to (13).

$$k_{\exp} = k_{n\mathrm{Br}}[\mathrm{Br}^-] \quad (13)$$

Rate constants. Fig. 4a shows plots of the observed rate constants *vs.* the concentration of entering bromide at constant concentration of chloride for reaction (4) starting from $\mathrm{AuCl_4^-}$. According to eqn. (12) the slopes give the rate constant for substitution of chloride by bromide, $k_{0\mathrm{Br}}$, and the intercepts the term $k_{0\mathrm{Cl}}[\mathrm{Cl}^-]$. Fig. 4b shows the linear plot of the intercepts *vs.* the chloride concentration, the slope of which gives $k_{0\mathrm{Cl}}$. Finally, Fig. 4c, shows a plot of the observed rate constants *vs.* the entering chloride concentration at various concentrations of bromide when reaction (4) is followed in the other direction, starting from a mixture of $\mathrm{AuCl_3Br^-}$ and $\mathrm{AuCl_4^-}$.

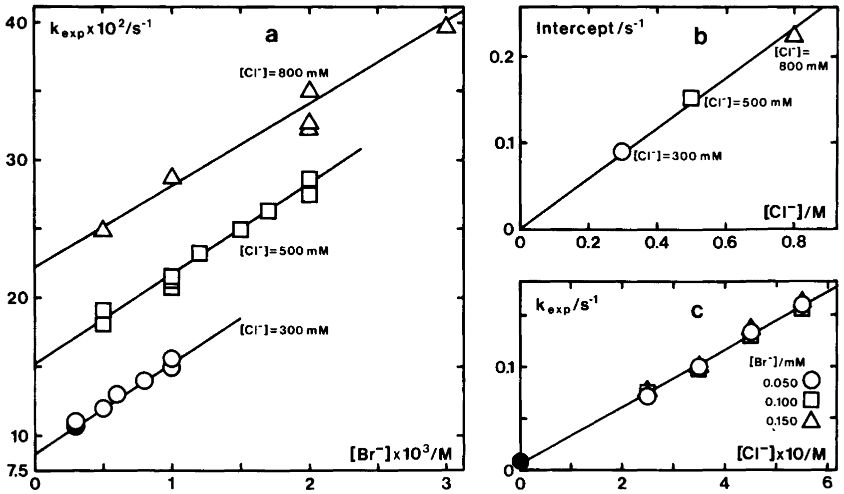


Fig. 4. Reaction (4) followed in the forward direction (a) and in the reverse direction (c). In (b), the intercepts from Fig. 4a have been plotted *vs.* $[\mathrm{Cl}^-]$. The symbol ● in Fig. 4c denotes $k_{0\mathrm{Br}} \times [\mathrm{Br}^-]$, for $[\mathrm{Br}^-] = 0.1$ mM, using the $k_{0\mathrm{Br}}$ value from Table 4.

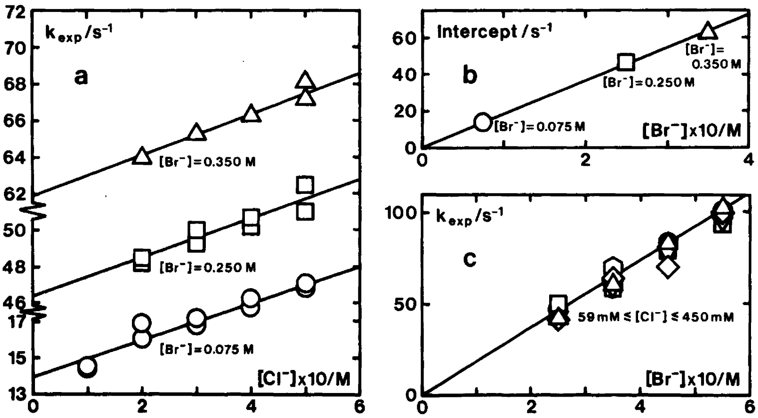


Fig. 5. Reaction (5) followed in the forward direction (c), and in the reverse direction (a). In (b), the intercepts from Fig. 5a have been plotted *vs.* [Br⁻].

The slope gives also a value for the rate constant k_{0Cl}.

Fig. 5 shows analogous plots for reaction (5). Fig. 5a gives k_{3Cl} from the slopes and $k_{3Br}[Br^-]$ from the intercepts according to eqn. (12), and Fig 5b gives k_{3Br}. The slope of the plot in Fig. 5c gives k_{3Br} according to eqn. (12), and the intercept $k_{3Cl}[Cl^-]$ is too small to be observable in this case.

Fig. 6 shows plots of the observed rate constants *vs.* the concentration of entering bromide for reactions (6) to (8), the slopes of which give k_{1tBr}, k_{2tBr} and k_{2cBr}, respectively, according to eqn. (13).

The rate constants are given in Table 4. Comparisons of the statistically corrected values of k/m using the relation $k/m = (const)TC_1C_2$ as described in Ref. 5, p. 15 give values of the relative *cis*- and *trans*-effects for these reactions. The reaction pairs

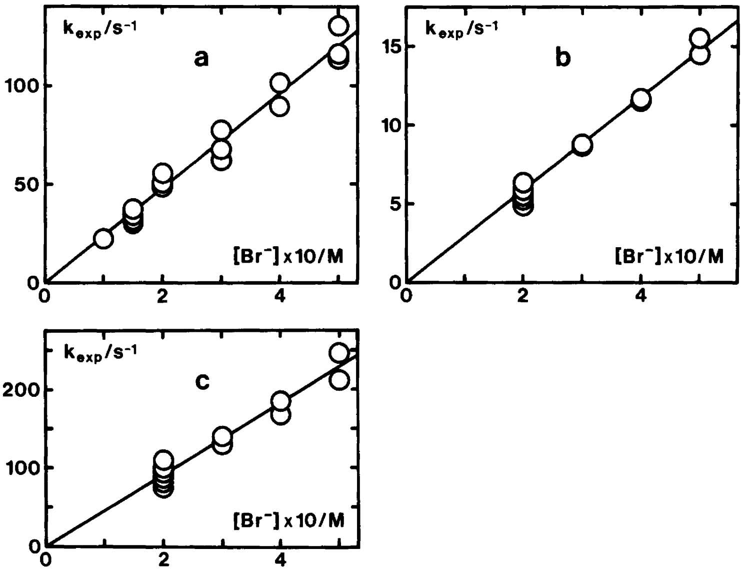


Fig. 6. Reactions (6)–a, (7)–b and (8)–c.

Table 4. Rate constants at 25 °C, 1.00 M perchlorate medium for reactions of gold(III) and platinum(II)[5] complexes.

Reaction	Rate constant	M = Au			M = Pt	$10^{-6}k_{Au}/k_{Pt}$
		k_{Au}/s^{-1} M^{-1}	$(k_{Au}/m)/s^{-1}$ $M^{-1\,a}$	Method	$10^5k_{Pt}/s^{-1}$ M^{-1} Ref. 5	
A $MCl_4^- + Br^- \rightarrow MCl_3Br^- + Cl^-$	k_{0Br}	63.3 ± 2.3	16	Fig. 4a	4.8	1.3
B $MCl_3Br^- + Br^- \rightarrow t\text{-}MCl_2Br_2^- + Cl^-$	k_{1tBr}	240 ± 20	240	Fig. 6a	8.9	2.7
C $MCl_3Br^- + Br^- \rightarrow c\text{-}MCl_2Br_2^- + Cl^-$	k_{1cBr}	29	14.5	Calc.[b]	2.6	1.1
D $t\text{-}MCl_2Br_2^- + Br^- \rightarrow MClBr_3^- + Cl^-$	k_{2tBr}	29.5 ± 1.5	14.8	Fig. 6b	0.94	3.1
E $c\text{-}MCl_2Br_2^- + Br^- \rightarrow MClBr_3^- + Cl^-$	k_{2cBr}	456 ± 40	228	Fig. 6c	10.0	4.6
F $MClBr_3^- + Br^- \rightarrow MBr_4^- + Cl^-$	k_{3Br}	185 ± 13	185	Fig. 5b, c	2.8	5.8
G $MCl_3Br^- + Cl^- \rightarrow MCl_4^- + Br^-$	k_{0Cl}	0.26 ± 0.03	0.26	Fig. 4b, c	0.45	0.056
H $t\text{-}MCl_2Br_2^- + Cl^- \rightarrow MCl_3Br^- + Br^-$	k_{1tCl}	7.0	3.5	Calc.[c]	4.2	0.13
I $c\text{-}MCl_2Br_2^- + Cl^- \rightarrow MCl_3Br^- + Br^-$	k_{1cCl}	0.45	0.23	Calc.[c]	0.60	0.075
K $MClBr_3^- + Cl^- \rightarrow t\text{-}MCl_2Br_2^- + Br^-$	k_{2tCl}	0.19	0.19	Calc.[c]	0.15	0.113
L $MClBr_3^- + Cl^- \rightarrow c\text{-}MCl_2Br_2^- + Br^-$	k_{2cCl}	6.2	6.2	Calc.[c]	3.1	0.174
M $MBr_4^- + Cl^- \rightarrow MClBr_3^- + Br^-$	k_{3Cl}	10.7 ± 2.5	2.7	Fig. 5a	3.0	0.38

[a] *m* is a statistical factor, equal to the number of equivalent leaving ligands in the complex. [b] Calculated from reactions A and F and the relative *cis*- and *trans*-effects Br^-/Cl^-. [c] Calculated from reactions G and M and the relative *cis*- and *trans*-effects Br^-/Cl^-, see text.

A;D, B;E and B;F indicate a relative *cis*-effect Cl^-/Br^- of $1,1 \pm 0.1$. Similarly, reactions B;A, D;F and, if corrections for the *cis*-effects are applied, reactions G;M, E;A, F;A and B;D give a relative *trans*-effect Br^-/Cl^- of 14 ± 3. Both the relative *cis*- and *trans*-effects are of the same order of magnitude as those found for the corresponding platinum(II) complexes.[5]

The acid hydrolysis rate constant for $AuCl_4^-$ is 2.2×10^{-2} s^{-1},[11,12] and for $AuBr_4^-$ 0.25 s^{-1} [2] at 25 °C. If these two rate constants are corrected for the difference in *cis*- and *trans*-effect between chloride and bromide, it appears that there is no difference between chloride and bromide as leaving groups in these complexes. This is also valid for the Pt(II)[5] and Pd(II)[13] complexes. A comparison of *k*/*m* for reactions A and G, and F and M, therefore shows that bromide is about 65 ± 5 times better as entering ligand than chloride in the gold complexes, compared to a factor of only about 3 for the corresponding platinum(II) complexes.[5]

The relative *cis*- and *trans*-effects obtained as described above were used to calculate rate constants for reactions C, H, I, K and L in Table 4, which are not accessible experimentally.

Reaction mechanism and reactivities. Fig. 7 reviews the system. Obviously, the over-all process (1) occurs mainly *via* the intermediate complexes $AuCl_3Br^-$, *trans*-$AuCl_2Br_2^-$ and $AuClBr_3^-$. The reaction *via* the *cis*-isomer contributes only with about 10 % to the over-all reaction ($k_{1cBr}/k_{1tBr} \approx 0.1$). In this respect there is a close similarity to

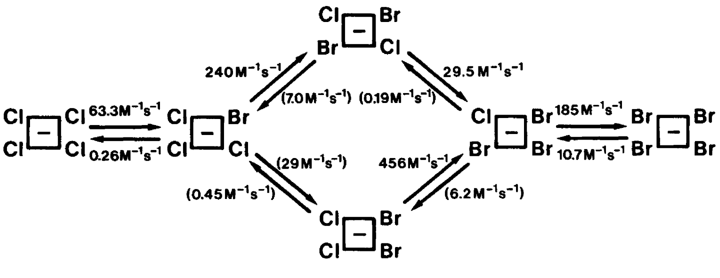


Fig. 7. Rate constants. Values within parenthesis calculated using relative *cis*- and *trans*-effects.

the analogous Pt(II)-system, *cf.* Ref. 5, Fig. 6. In the case of gold, however, each substitution step takes place *via* a direct halide exchange, the solvent path (the k_1-term[4]) being completely negligible. The halide substitutions in the platinum complexes, on the other hand, occur *via* the usual two-term rate law,[4] the solvent path often being the predominant contributor to the over-all rate for the halide concentration ranges accessible.[5]

Table 4 gives a comparison of the reactivities of analogous gold(III) and platinum(II) complexes. For bromide as entering ligand the former react about 2×10^6 times faster than the latter, and for chloride as entering ligand about 10^5 times faster. The difference in relative reactivity by a factor of about 20 ($2 \times 10^6/10^5$) shows that the nature of the entering ligand is more important for reactions of the gold complexes than for those of the platinum complexes. (This is equivalent to the conclusion in the previous paragraph that bromide is 65 times better as entering ligand than chloride for gold, but only about 3 times better for platinum complexes).

Whereas there is no difference between chloride and bromide as leaving ligands in the gold complexes, a comparison of the rate constant 2.3×10^3 s^{-1} M^{-1} (Bekker and Robb[14]) for the reaction between $AuCl_3H_2O$ and chloride, and the rate constant 1.5 s^{-1} M^{-1} (Rich and Taube[15]) for the isotopic exchange of chloride in $AuCl_4^-$, corrected for the differences in ionic charge (*cf.* Ref. 5), shows that water is about 300 times – $2.3 \times 10^3/(5 \times 1.5)$ – better as leaving ligand than chloride. Thus, the influence of the leaving group (Cl, Br, H_2O) appears to be similar for gold(III) and platinum(II) complexes (*cf.* Ref. 5).

The absence of an observable solvent path in the present experiments on the gold complexes is also in accord with the increased importance of the nature of the entering group in the case of gold. The rate constants for the acid hydrolyses ($M = Au, Pt; j = 1, 2$)

$$MCl_4^{j-} + H_2O \xrightarrow{k_1} MCl_3OH_2^{1-j} + Cl^-$$

$$MBr_4^{j-} + H_2O \xrightarrow{k_2} MBr_3OH_2^{1-j} + Br^-$$

are $k_{1Au} = 0.022$ s^{-1},[11] $k_{1Pt} = 4 \times 10^{-5}$ s^{-1},[5] $k_{2Au} = 0.245$ s^{-1},[2] and $k_{2Pt} = 19 \times 10^{-5}$ s^{-1},[5] which give $k_{1Au}/k_{1Pt} = 6 \times 10^2$ and $k_{2Au}/k_{2Pt} = 12 \times 10^2$. For water as entering ligand the ratio in reactivity between gold and platinum is obviously only about 10^3. Summarizing:

Entering ligand	k_{Au}/k_{Pt}
H_2O	$\sim 10^3$
Cl^-	$\sim 10^5$
Br^-	$\sim 2 \times 10^6$

The relative contribution of the solvent path to the over-all reaction is thus 100 to 1000 times smaller for the gold complexes than for those of platinum when halide is the entering ligand.

These observations support the picture of an associative intimate mechanism and are compatible with Baddley's and Basolo's[16] conclusion that bond formation in the transition state is more important for gold(III) than for platinum(II) complexes.

The four rate constants $k_{0Br} = 63.3$ M^{-1} s^{-1}, $k_{1tBr} = 240$ M^{-1} s^{-1}, $k_{2tBr} = 29.5$ M^{-1} s^{-1} and $k_{3Br} = 185$ M^{-1} s^{-1} are so close to each other that the four consecutive reactions in the gold system are not kinetically separated in aqueous solution (*cf.* Fig. 7). If this is valid for methanol solution also, the experiments in Ref. 1, evaluated using a model with two separated rate-determining steps, might give too large values for the rate constants of the first, rapid step. The intercepts of the k_{obs} *vs.* [Y] plots might then be due to a deviation from first-order kinetics, caused by the two consecutive reactions $AuCl_4^- \rightarrow AuCl_3Br^- \rightarrow$ *trans*-$AuCl_2Br_2^-$, and not by a reaction with the solvent. The rather large scatter in the values of the intercepts for different entering ligands Y, $(2.7 \pm 2.1) \times 10^{-3}$ s^{-1}, support this interpretation.

The results in Fig. 7 show clearly that the "single-stage" reaction observed in Ref. 2 is composed of a series of consecutive processes. To treat these consecutive reactions as a first-order process will of course give rate constants, which have no physical significance. A variation of wavelength shows immediately the complexity of the reaction. For the experimental conditions used in Ref. 2, there is a monotonous increase of absorbance at 382 nm, which might be misinterpreted as one reaction, whereas at 300 nm, there is first a rapid decrease, followed by a slower increase, *cf.* Fig. 2.

The equilibrium constants in Table 5 and the graphical representation in Fig. 8 show, that for the chloride and bromide concentrations used in the experiments by Hall and Satchell,[3] $AuClBr_3^-$ and $AuBr_4^-$ will be the products at equilibrium. Spectra of equilibrated solutions are not identical with the $AuCl_3Br^-$ spectrum (see Fig. 3) as assumed by these authors. One single wavelength (nominal 312 nm) was used for all their experiments. Our spectra

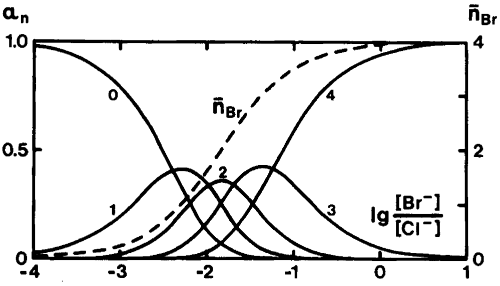


Fig. 8. The distribution of gold between the species $AuCl_{4-n}Br_n^-$, $n=0$, 1, 2, 3, 4 for 25 °C and 1.00 M perchlorate medium calculated from the equilibrium constants in Table 5.

Table 5. Stepwise equilibrium constants, K_n, defined by eqn. (3).

K_n	From kinetics 1 M $NaClO_4$	From Ref. 17 3 M $HClO_4$
K_0	243 ± 40	288
K_1	98 ± 20	135
K_{1c}	64 ± 13	90[a]
K_{1t}	34 ± 7	45[a]
K_2	49 ± 10	64.6
K_{2c}	73 ± 15	97[a]
K_{2t}	153 ± 30	194[a]
K_3	17 ± 5	23.4

[a] Calculated, assuming a statistical distribution ' [*cis*]/[*trans*] = 2:1.

in Fig. 3 show that at 320 nm, for instance, the absorbance will first increase due to formation of $AuCl_3Br^-$ and $AuCl_2Br_2^-$, and then decrease, when $AuClBr_3^-$ and $AuBr_4^-$ are formed. This is exactly what was observed in Ref. 3. A systematic wavelength error of 8 nm is not at all unusual for a Durrum-Gibson instrument. Experiments performed at other wavelengths, for instance at 382 nm – *cf.* Fig. 2 – immediately show that the mechanistic interpretation made in Ref. 3 cannot be correct.

The "chloride catalysis" reported by Hall and Satchell[3] is also compatible with the model in Fig. 7, the reactions studied being reversible, and the back reactions being chloride dependent; *cf.* eqn. (12). Finally, it seems very unlikely that the rate of formation of a five-coordinate adduct between $AuCl_4^-$ and bromide of the type proposed in Ref. 3 should lie within the stopped-flow region.

Equilibria. The equilibrium constants K_n, $n=0$, 1, 2, 3, given in Table 5 were calculated from the rate constants in Table 4 using eqn. (3). They agree satisfactorily with those previously calculated by Almgren[17] from spectrophotometric equilibrium measurements for a 3 M perchlorate medium. The values of $K_{1c}/K_{1t}=1.9\pm0.7$ and $K_{2t}/K_{2c}=2.1\pm0.8$ indicate that the two isomers of $AuCl_2Br_2^-$ are present at equilibrium in about the statistically expected ratio [*cis*]/[*trans*] = 2:1, which is also a reasonable result. Fig. 8 shows the distribution of gold between the different complexes calculated from these constants. Table 6 shows that the distribution is very nearly statistical.

The equilibrium constants K_n defined by eqn. (3) are related to the over-all stability constants β_{4X} for the chloro and bromo complexes, defined by eqn. (14), by the relation (15).

$$\beta_{4X}=\frac{[AuX_4^-]}{[Au^{3+}][X^-]^4} \tag{14}$$

$$K_0K_1K_2K_3=\beta_{4Br}/\beta_{4Cl} \tag{15}$$

The constants in Table 5 give $\beta_{4Br}/\beta_{4Cl}=2.0\times10^7$ which is compatible with J. Bjerrum's and Skibsted's[18] calculation log $\beta_{4Cl}=26$ and log $\beta_{4Br}=34$ (*cf.* also Refs. 19, 20, 21). Thus, the difference in stability between the bromo and chloro complexes of gold(III) is much larger than the difference for the corresponding platinum(II) complexes, having

Table 6. Statistical and experimental values for the equilibrium constants of the mixed complexes formed from $AuCl_4^-$ and $AuBr_4^-$.

Reaction	lg K (found)	lg K (statistical)
$3/4\ AuCl_4^- + 1/4\ AuBr_4^- \rightleftharpoons AuCl_3Br^-$	0.56	0.60
$1/2\ AuCl_4^- + 1/2\ AuBr_4^- \rightleftharpoons AuCl_2Br_2^-$	0.73	0.78
$1/4\ AuCl_4^- + 3/4\ AuBr_4^- \rightleftharpoons AuClBr_3^-$	0.59	0.60

Table 7. Wavenumbers, $\lambda^{-1}/\mu m^{-1}$; molar absorptivities, $\varepsilon_n/cm^{-1}M^{-1}$, for $AuCl_{4-n}Br_n^-$, ($n=0$, 1, 2, 3, 4) and proposed assignments for D_{4h} symmetry.

Peak	$AuCl_4^-$	$AuCl_3Br^-$	$AuCl_2Br_2^-$	$AuClBr_3^-$	$AuBr_4^-$	Assignment(D_{4h})	Excited state (D_{4h})
a	~2.25(70)	–	–	–	–	$d-d$	
b	2.52(350)	2.31(400)	2.15(400)	~2.0(300)	1.83(200)	$3b_{1g}\leftarrow a_{2g}$	$^1B_{2g}$ (allowed *via* E_u-vibration)
c	–	2.63(800)	2.49(1200)	2.40(1350)	2.21(1350)	$3b_{1g}\leftarrow 3e_u$	^3E_u
d	3.19(5500)	3.05(5500)	3.00(6800)	2.83(4850)	2.62(4950)	$3b_{1g}\leftarrow 3e_u$	^1E_u
e	–	~3.7(800)	3.60(1000)	3.52(1400)	~3.4(1800)	?[a]	–
f	4.39(37500)	4.26(42000)	4.13(34500)	4.03(43500)	3.92(44000)	$3b_{1g}\leftarrow 2e_u$	^1E_u

[a] See footnote g in Table V of Ref. 22, alternatively $3b_{1g}\leftarrow 2e_u$ (^3E_u), *cf.* Table III of Ref. 22.

$\beta_{4Br}/\beta_{4Cl} = 133 \pm 15$.[5] In other words, gold(III) is an extremely soft metal.

Spectra. The charge-transfer spectra of $AuCl_4^-$ and $AuBr_4^-$ shown in Fig. 3 are very similar to those of the corresponding Pd(II) complexes,[22] the bands of the gold complexes being displaced somewhat more towards the visible region. Table 7 gives tentative assignments, which are analogous to those proposed for $PdCl_4^{2-}$ and $PdBr_4^{2-}$.[22] The assignments for bands *d* and *f* agree with those made previously by Chakravorty *et al.*[23] The $d-d$ bands of the gold complexes are difficult to observe because of their proximity to the high-intensity bands. The band denoted by *b* in Table 7 has a rather large intensity in all the complexes and blue-shifts approximately the same as bands *c* to *f*, so it has been classified as a charge-transfer band (*cf.* Ref. 22).

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