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Kinetics and Mechanisms of Reactions of Gold(III) Complexes. II. The Formation and Equilibrium Hydrolysis of Tetrabromoaurate(III)

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The first two hydrolysis steps of the tetrabromoaurate(III) ion have been studied over a range of temperature and bromide and hydrogen ion concentrations. Both steps follow the normal two-term rate law for square planar equilibrium solvolysis, with a direct hydrogen ion concentration dependence incorporated in the second order term. In the formation of tetrabromoaurate(III) from tetrachloroaurate(III) only one reaction was observed. On the basis of the experimental data this appears to be the displacement of the first chloride.

Introduction

The stability of platinum(II) complexes has allowed a wide variety of substitution reactions to be studied on these substrates.[1] Attempts to extend these studies to the isoelectronic gold(III) compounds were limited by the general ease of reduction and lability of gold(III) complexes. The fast hydrolysis of the tetrahaloaurate (III) complexes[2] yielded various substrates in solution and thus complicated the study of their substitution reactions. Previous workers have managed to solve this problem in two ways: 1) $Au(dien)X^{2+}$ (X = halide or pseudo halide) was used as a substrate,[3] thus blocking the hydrolysis, and 2) solvents were used in which the solvolysis rate was slow.[4,5] In our study on the hydrolysis of $AuBr_4^-$ and formation of $AuBr_4^-$ from $AuCl_4^-$, we have overcome the lability problem of these Au^{III} ions by exploiting the enormous extinction coefficients of $AuCl_4^-$ ($\varepsilon = 42{,}500$ l mole^{-1} cm^{-1} in CH_3CN) and $AuBr_4^-$ ($\varepsilon = 33{,}000$ l mole^{-1} cm^{-1} in CH_3CN).[6,7] Thus by decreasing the Au^{III} anion as well as ligand concentrations in the reacting solution, the reaction rate was slowed down sufficiently and enabled the spectrophotometric detection of the $AuBr_4^-$ hydrolysis and its formation reaction from $AuCl_4^-$.

Experimental

Materials

The $KAuBr_4$ complex was prepared as reported in 'Inorganic Synthesis'.[8] However, if the preparative steps are not carefully followed, the product analyses for the dimer, Au_2Br_6. $HAuBr_4$ was also prepared by adding an excess of Br^- to an aqueous solution of $HAuCl_4^-$, then extracting the $HAuBr_4$ formed in ether and evaporating the solution to dryness under reduced pressure. Its purity was tested by comparing its U.V.–visible spectrum with those previously reported.[6,7]

Kinetics

All the normal buffers used in a pH range 0–5, e.g. acetate, phosphate and phthalate, react with $AuBr_4^-$. The reaction solutions were therefore unbuffered, and the pH was adjusted with a few drops of diluted perchloric acid. Since the ionic strength was kept constant at 0.1 with $NaClO_4$, and the $AuBr_4^-$ and $AuCl_4^-$ concentrations were approximately $10^{-5}M$, no pH change due to possible deprotonation of $AuCl_3(H_2O)$ was detected during the reactions. However, with much more concentrated solutions a pH change is observed. The pH and ionic strength of a $10^{-3}M$ NaBr solution were adjusted in the same manner.

It was possible to follow the hydrolysis and formation reactions spectrophotometrically on a Cary–15 by focussing on the 254 nm and 226 nm peaks of the $AuBr_4^-$ and $AuCl_4^-$ U.V. spectra, respectively. In order to improve the absorption, 20 mm cells were used. Normal thermostating was applied. The hydrolysis reaction was studied by a relaxation technique, and entailed disturbing of the $AuBr_4^-$ equilibrium solution by rapidly injecting the bromide solution with a syringe. The same technique was utilized for studying the formation of $AuBr_4^-$ from $AuCl_4^-$.

Hydrogen ion concentrations were measured with a Metrohm Model E300 pH meter.

Results and Discussion

The Hydrolysis of $AuBr_4^-$

The results obtained from the U.V. spectra of aqueous solutions of $AuBr_4^-$ ($\cong 10^{-3}M$) in the presence of different bromide ion concentrations indicated that a reversible hydrolysis was being observed. When the $[Br^-]$ was increased, the absorption moved towards 380 nm and the peak height increased. The pH values of these solutions also increased with increasing bromide ion concentration. This suggests a deprotonation of the hydrolysis product species.

Four consecutive reactions were observed in the $AuBr_4^-$ equilibrium hydrolysis, with the first two being very fast. The rate of the four reactions were such that 'stripping' of the plots of optical density *vs* time of all four reactions had to be undertaken in order to obtain the separate reaction plots. This, however, was very unsatisfactory. The alternative method hence used to separate the reactions was to take the optical density values at five half-lives for the first and second reactions as the equilibrium values. Using these results, the straight lines obtained from the plots of $\log(OD_t - OD_e)$ *vs* time were much more satisfactory. Because the optical density change was too small, the third reaction could not be dissociated successfully from the fourth reaction which showed no dependence on either $[Br^-]$ or complex ion concentration.

The first two reactions both obeyed the general two-term rate law for square planar equilibrium solvolysis,[1] the only difference being the presence of a direct $[H^+]$ term incorporated in both of the second order terms, *viz.*

$$k_{obs_1} = k_1 + \frac{k_{-1}[Br^-][H^+]}{K_a} \qquad (1)$$

$$k_{obs_2} = k_2 + \frac{k_{-2}[Br^-][H^+]}{K_a'} \qquad (2)$$

These rate laws are derived from the following reaction scheme which is in agreement with all the above mentioned experimental data.

$$\begin{tikzcd}
AuBr_4^- + H_2O \arrow[r, shift left, "k_1"] & AuBr_3(H_2O) + Br^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "K_a"] & AuBr_3(OH)^- + H^+ \arrow[l, shift left] \arrow[d, shift right, "k_2"'] \\
& AuBr_2(OH)_2^- + H^+ \arrow[r, shift left, "K_a'"] & AuBr_2(H_2O)(OH) + Br^- \arrow[l, shift left] \arrow[u, shift right, "k_{-2}"']
\end{tikzcd}$$

No evidence was found for any redox-catalysed substitution reaction of the kind found by Rich and Taube.[9] Reduction to gold metal only occurred when the AuX_4^-

TABLE I. $[Br^-]$ and $[H^+]$ dependence of first-order rate constants at 15° C and $\mu = 0.1$ for the reaction

$$AuBr_4^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AuBr_3(H_2O) + Cl^-.$$

$[Br^-]$ $M \times 10^4$	pH	k_{obs}[a] sec^{-1}
1.25	3.3	.6
2.0	3.3	.75
1.25	3.5	.58
2.5	3.5	.795
2.0	3.5	.65
1.25	3.7	.346
2.0	3.7	.425
2.5	3.7	.495
3.3	3.7	.615
4.0	3.7	.693
4.0	3.8	.66
3.3	3.8	.58
2.5	3.8	.495
2.0	3.8	.405
1.25	3.8	.295
2.0	4.0	.314
2.5	4.0	.346
3.3	4.0	.385
4.0	4.0	.46
5.0	4.0	.535
1.25	4.2	.21
2.0	4.2	.24
3.3	4.2	.3
5.0	4.2	.364

[a] Average of up to 7 values.

TABLE II. Temperature dependence of first-order rate constants at pH 3.7 and $\mu = 0.1$ for the reaction

$$AuBr_4^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AuBr_3(H_2O) + Cl^-.$$

$[Br^-]$ $M \times 10^4$	Temperature °C	k_{obs}[a] sec^{-1}
1.25	20	.4
1.43	20	.415
2.0	20	.535
2.5	20	.61
3.3	20	.75
1.25	15	.35
2.0	15	.44
2.5	15	.535
3.3	15	.65
4.0	15	.74
1.25	10	.28
2.0	10	.38
2.5	10	.45
3.3	10	.56
4.0	10	.63
1.25	5	.243
2.0	5	.33
2.5	5	.385
3.3	5	.48

[a] Average of up to 7 values.

TABLE III. Rate constants and activation parameters for the reaction $AuBr_4^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AuBr_3(H_2O) + Br^-$.

Temperature °C	k_1 sec^{-1}	k_{-1}/K_a $sec^{-1}M^{-2} \times 10^{-6}$	K_ak_1/k_{-1} $\times 10^9$	k_1/k_{-1} $M \times 10^6$	k_{-1} $sec^{-1}M^{-1} \times 10^{-4}$
1	–	–	9.5[b]	–	–
5	0.104	5.7	18.2	–	4.6
10	0.13	6.3	20	–	5.0
15	0.16	7.4	21.6	–	5.9
20	0.2	8.3	24.1	–	6.6
25	0.245[a]	9.5[a]	25.8[e]	3.4[c]	7.6

	k_1	k_{-1}
E_a kcal mol^{-1}	6.9	4
$\Delta H^{\ddagger}$ kcal mol^{-1}	6.3	3.4
$\Delta S^{\ddagger}$ eu	–40	–23.7
$\Delta F^{\ddagger}$ kcal mol^{-1}	18.3	10.6

[a] extrapolated. [b] value from Ref. 12. [c] value from Ref. 11. [d] $K_a = 0.8 \times 10^{-2}$ from e/c.

solutions were allowed to stand in light for more than a week. Although dimers were frequently encountered in the preparation of $AuBr_4^-$, no evidence of their existence in solution or participation in the reactions was found, as have been observed during the hydrolysis reaction of $PtBr_4^{2-}$,[16] or with a non-aqueous $AuBr_4^-$ solution in the presence of exccss Br^-.[10]

Tables I and IV show the $[Br^-]$ and $[H^+]$ dependence of reactions 1 and 2, respectively, while Tables II and V list the temperature dependence, and Tables III and VI the rate constants and activation parameters.

Table III also list K_ak_1/k_{-1}[12] and k_1/k_{-1}[11] values measured by other workers in equilibrium studies. The equilibrium constant for the first hydrolysis reaction of $AuBr_4^-$ measured by Kazakov 9.5×10^{-9} at 1° C[12] (deprotonation of $AuBr_3(H_2O)$ included in equilibrium) is comparable with our value of 18.2×10^{-9}

TABLE IV. $[Br^-]$ and $[H^+]$ dependence of first-order rate constant at 20° C and $\mu = 0.1$ for the reaction

$AuBr_3(OH)^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AuBr_2(OH)(H_2O) + Cl^-$.

$[Br^-]$ $M \times 10^3$	pH	k_{obs}[a] $sec^{-1} \times 10^2$
2.0	3.6	7.1
2.5	3.6	7.6
3.3	3.6	9.65
4.0	3.6	11.0
5.0	3.6	11.75
6.0	3.6	14.5
6.6	3.6	15.5
2.0	4.4	2.7
4.0	4.4	3.2
5.0	4.4	3.4
6.0	4.4	3.75
2.0	4.0	4.5
3.3	4.0	6.2
5.0	4.0	7.5
6.6	4.0	9.1

[a] Average of up to 4 values.

TABLE V. Temperature dependence of first-order rate constant at pH 4.0 and $\mu = 0.1$ for the reaction

$AuBr_3(OH)^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AuBr_2(OH)(H_2O) + Cl^-$.

$[Br^-]$ $M \times 10^3$	Temp. °C	k_{obs}[a] $sec^{-1} \times 10^2$
2.0	15	3.4
3.3	15	4.3
4.0	15	5.0
5.0	15	5.8
6.0	15	6.4
6.6	15	7.2
2.0	20	4.6
3.3	20	6.0
4.0	20	6.3
5.0	20	7.5
6.0	20	8.7
6.6	20	9.4
2.0	25	7.2
2.5	25	8.4
3.3	25	8.6
4.0	25	10
5.0	25	10.8
6.0	25	12.6
6.6	25	13.3
2.0	30	8.75
2.5	30	10.0
3.3	30	11.5
4.0	30	13
5.0	30	14.4
6.0	30	15.5

[a] Average of up to 5 values.

TABLE VI. Rate constants and activation parameters for the reaction $AuBr_3(OH)^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AuBr_2(OH)(H_2O) + Cl^-$.

Temperature °C	k_2 sec^{-1} × 10^2	k_{-2} sec^{-1} M^{-1}
15	1.75	8
20	2.5	10.3
25	4	14.0
30	5.6	17.6
E_a kcal mol^{-1}	13.2	9.2
$\Delta H^{\neq}$ kcal mol^{-1}	12.6	8.6
$\Delta S^{\neq}$ eu	–23	–24
$\Delta F^{\neq}$ kcal mol^{-1}	19.4	15.9

[a] K_a' estimated as 10^{-4}.

TABLE VII. [Br$^-$] and temperature dependence of the first-order rate constants at pH 4.2 and $\mu = 0.1$ for the reaction $AuCl_4^- + Br^- \rightarrow$.

[Br$^-$] M × 10^3	Temperature °C	k_{obs}[a] sec^{-1} × 10^2
2.0	25	5.7
2.5	25	6.3
3.3	25	8.55
4.0	25	9.65
5.0	25	11.4
6.0	25	12.9
2.0	20	4.75
2.5	20	5.75
3.3	20	6.6
4.0	20	7.9
5.0	20	9.35
6.0	20	10.9
2.0	30	8.35
2.5	30	9.35
3.3	30	11.35
4.0	30	12.85
5.0	30	15

[a] Average of up to 4 values.

The availability of the k_1/k_{-1} value[11] enabled the calculation of the K_a value for $AuBr_3(H_2O)$ of 0.8×10^{-2}.

An attempt was made to measure the hydrolysis reaction in 1M $HClO_4$ with a stopped-flow apparatus, as has been done previously in this laboratory with the $AuCl_4^-$ hydrolysis.[14] With the $HClO_4$ acid concentration of 1M the deprotonation of $AuBr_3(H_2O)$ was suppressed and k_{-1} could be measured directly. However, using $10^{-5}M$ $AuBr_4^-$ and $5 \times 10^{-2}M$ Br^- solution the reaction was too fast to measure (faster than 1 msec). A lower limit of 10^4 sec$^{-1}M^{-1}$ can therefore be put on the k_{-1} value, and similarly a lower limit of 10^{-3} for the K_a value. It appears that these limits are very close to the calculated values, utilizing the published k_1/k_{-1} value.

The $AuCl_4^-$ + Br^- Reaction

Only a single stage reaction occurred that obeyed the normal square planar substitution rate law:

$$k_{obs} = k_s + k_y [Br^-] \qquad (3)$$

The experimental data are listed in Tables VII and VIII. The initial spectra correspond to that of $AuCl_4^-$ and the final reaction spectra to that of pure $AuBr_4^-$. Exactly the same behaviour was found by Cattalini[5] for the reactions:

$$AuCl_4^- + Y^- \xrightarrow{CH_3OH}$$

with Y = I and SCN, but the reaction was reported to occur in two steps with Y = Br as the nucleophile. In all three cases the replacement of the first chloride ion was a rate-determining step. The good agreement between the k_s values obtained from this study and from the $AuCl_4^-$ hydrolysis[2] (Table VIII) suggests that the replacement of the first chloride ion is also the rate-determining step in water solution. Similar results have been reported for the reaction of $PtCl_4^{2-}$ with Br^- in water.[15]

TABLE VIII. Rate constants and activation parameters for the reaction $AuCl_4^- + Br^- \rightarrow$.

Temperature °C	k_s sec^{-1} × 10^2		k_s[a] sec^{-1} × 10^2	k_y sec^{-1} M^{-1}
20	1.6	(20.5° C)	1.4	15.4
25	2.3		2.2	18.2
30	3.5	(30.4° C)	3.3	23.2
E_a kcal mol^{-1}	13.3		16.1	7.3
$\Delta H^{\neq}$ kcal mol^{-1}	12.7		15.5	6.7
$\Delta S^{\neq}$ eu	–23		–15	–30
$\Delta F^{\neq}$ kcal mol^{-1}	19.7		19.7	15.7

[a] $AuCl_4^-$ hydrolysis rate constant values taken from Ref. 2.

TABLE IX. Rate constants for some gold (III) and platinum (II) complex reactions.

Complex	H_2O sec^{-1}	Cl^- sec$^{-1}M^{-1}$	Br^- sec$^{-1}M^{-1}$
$AuCl_4^-$ [a]	2.2×10^{-2}	1.47 (20° C)	18.2 (15.4, 20° C)
	5×10^{-4} (CH_3OH the solvent)	–	0.14 (CH_3OH)
$AuCl_3(H_2O)$[a]	–	2.32×10^3	–
$AuCl_3Br^-$ [b]	–	5×10^{-2}(20° C)	–
$AuBr_4^-$	2.45×10^{-1}	–	–
$AuBr_3(H_2O)$	–	–	7.6×10^4
$PtCl_4^{2-}$ [c]	5×10^{-5}	–	4×10^{-4}
$PtBr_4^{2-}$ [d]	2.2×10^{-4}	-	-

[a] Ref. 2. [b] Calculated from k_y and the equilibrium constant published for $AuCl_4^- + Br^- \rightleftarrows AuCl_3Br^- + Cl^-$ in Ref. 13. [c] Ref. 15. [d] Ref. 16.

Comparison of the Kinetic Behaviour of gold(III) and Platinum(II) Complexes

Baddley and Basolo[3] originally proposed that bond formation in the rate-determining state is more important in gold(III) than in platinum(II). Cattalini and co-workers,[5] while supporting this, also showed the equal importance of bond breaking steps in Au^{III} systems. This is in agreement with the results obtained in this study. The ratio for the rate constants of the reactions:

$$AuCl_3X + Cl^- \rightarrow (X = H_2O, Cl^-, Br^-)$$

is $k_{Br^-} : k_{Cl^-} : k_{H_2O} = 1:29:4.7 \times 10^4$ whereas a similar ratio, only in decreasing order, is found when these nucleophiles are the incoming groups with $AuCl_4^-$ as substrate, *viz.* $k_{H_2O} : k_{Cl^-} : k_{Br^-} = 1:3.8 \times 10^2:4 \times 10^3$ (k_{H_2O} is divided by $55M$ in order to compare second-order rate constants). These ratios are in agreement with the *trans* series as is the much faster hydrolysis and anation of $AuBr_4^-$ compared to $AuCl_4^-$.

The $AuBr_4^-$ hydrolysis is about thousand times faster than the $PtBr_4^-$ hydrolysis,[16] which is thus analogous to the Au and Pt chloride systems.[2,15] The much larger rate constants observed in this study compared to those observed for the bromide substitution in $AuCl_4^-$ in CH_3OH[5] is to be expected when a higher dielectric solvent is used.

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