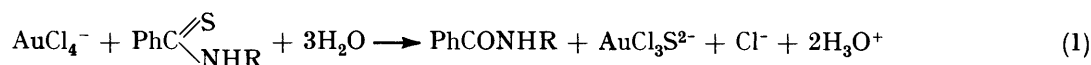# The Kinetics and Mechanism of Thioamide Hydrolysis promoted by Gold(III) Bromides in Aqueous Solution

By Jacob V. Micallef and Derek P. N. Satchell,* King's College, Strand, London WC2R 2LS

Kinetic and spectroscopic studies are reported of the reactions of N-cyclohexylthiobenzamide with the ions $AuBr_4^-$ and $trans$-$Au(CN)_2Br_2^-$ in aqueous solutions to give the corresponding O-benzamide. The effects of temperature, pH, ionic strength, and ambient bromide ion concentration are described and mechanisms for the reactions suggested. The reactions involve the rapid, stoicheiometric formation of S-amide–gold(III) ion adducts which decompose slowly to the O-amide. Comparison of the results with those of previous studies shows that, for square planar adducts, the rate of the desulphurisation process is increased by an increase in (i) the positive charge on the gold atom and (ii) the softness of the attached ligands. In the presence of added ambient bromide ions the gold ions and adducts are partially or completely converted into octahedral species. The desulphurisation process in the octahedral adducts is faster than in the square planar adducts.

WE have reported previously [1,2] on the kinetics and mechanism of the hydrolysis of S-benzamides in aqueous solution promoted by chlorogold(III) and various amino-chlorogold(III) ions [e.g. equation (1)]. We report now on the promotion of the hydrolysis of N-cyclohexylthio-benzamide by some bromogold(III) ions.

observed the subsequent decomposition of the rapidly formed adducts.

Kinetics.—These were studied, and rate constants evaluated, by methods previously described.[1,2] All reaction mixtures contained at least a 10-fold excess of the promoting ions and the S-amide was added as a solution in

$$AuCl_4^- + PhC\overset{S}{\underset{NHR}{\diagup}} + 3H_2O \longrightarrow PhCONHR + AuCl_3S^{2-} + Cl^- + 2H_3O^+ \qquad (1)$$

EXPERIMENTAL

Materials.—Potassium tetrabromoaurate (1) was the Johnson–Mathey product. *trans*-Potassium dibromodicyanoaurate (2) was prepared by the method of Smith *et al.*[3] It analysed correctly and had i.r. and u.v. spectra in agreement with reported values.[3,4] Water was doubly distilled. N-Cyclohexylthiobenzamide and the corresponding O-amide were previous samples. The remaining chemicals were the purest available commercial products.
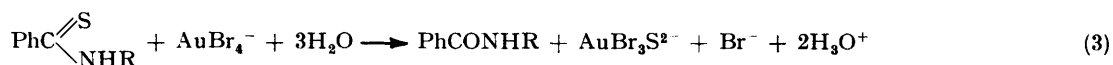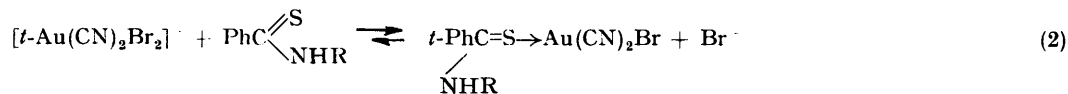
Adduct Formation.—Aqueous solutions of the promoting ions in the presence of the S-benzamide possess u.v. spectra which differ from those expected from the simple addition of the spectra of the components. This fact suggests the rapid formation of adducts between the S-amide and the gold species. Adduct stoicheiometries were investigated by Harvey and Manning's method.[5] We find that the *trans*-dibromodicyanoaurate forms a 1 : 1 adduct quantitatively with the S-amide under all the concentration conditions used in our kinetic experiments, probably as exemplified in equation (2). The stoicheiometry observed with the tetra-

ethanol. There occurs a substantial fall in absorption in the region 250—400 nm as the adducts decompose to give the O-amide. Reaction mixtures were free from gold sulphide precipitation throughout most of the course of the hydrolysis and A_∞ values observed were always within $\pm 8\%$ of those computed to fit the data best. The observed first-order rate constant, k_{obs}, for loss of adduct was reproducible to within $\pm 12\%$. During promotion by (2) in the absence of added bromide ions there occurs a small, relatively slow fall in absorption after adduct formation but prior to the start of O-amide formation. This unexplained affect is absent in the presence of added bromide ions. Our results for various conditions are in Tables 1 and 2.

Reaction Products.—Preparative-scale experiments using concentration conditions as close as practicable to those of the kinetic runs showed that the promoted hydrolyses led to the O-amide in high yield as the only organic product [e.g. reaction (3)]. The bromogold sulphide, which is presumably formed initially, undergoes further reactions and a brown precipitate containing gold and sulphur is eventually formed.

$$[t\text{-}Au(CN)_2Br_2]^- + PhC\overset{S}{\underset{NHR}{\diagup}} \rightleftharpoons t\text{-}PhC{=}S{\rightarrow}Au(CN)_2Br + Br^- \qquad (2)$$
$$\underset{NHR}{\diagup}$$

$$PhC\overset{S}{\underset{NHR}{\diagup}} + AuBr_4^- + 3H_2O \longrightarrow PhCONHR + AuBr_3S^{2-} + Br^- + 2H_3O^+ \qquad (3)$$

bromoaurate (at *ca.* 10^{-3}M) depends to some extent upon the ambient bromide ion concentration. When $[Br^-] \gtrsim 0.1$M, and $AuBr_4^-$ is not present in great excess over the S-amide, only 2 S-amide : 1 gold adducts are found; when $[Br^-] \lesssim 10^{-3}$M there probably exists a mixture of 2 : 1 and 3 S-amide : 1 gold adducts. In our kinetic experiments we

RESULTS AND DISCUSSION

Promotion by trans-*Potassium Dibromodicyanoaurate* (2).—The effects observed with this promoter are simpler than those found for the tetrabromide and will therefore be discussed first. Our kinetic results (Table 1) show

TABLE 1

Promotion by potassium dibromodicyanoaurate (2). [S-amide]$_{initial} \simeq 7 \times 10^{-5}$M; solvent 4% v/v ethanol-water; for k_{obs} see text; I = ionic strength; temperature = 25.0 °C unless stated otherwise

(i) Effect of bromide ion concentration {10^4[KAu(CN)$_2$Br$_2$] = 9.6M; 10^2[H$_3$O$^+$] = 9.6M; I = 0.92}
See Figure 1

(ii) Effect of hydrogen ion concentration when [Br$^-$] = 0 {10^4[KAu(CN)$_2$Br$_2$] = 9.7M; I = 0.24M}

10^2[H$_3$O$^+$]/M	0.00	0.040	0.10	0.20	0.47	1.00
$10^2 k_{obs}$/s^{-1}	1.2	1.1	0.84	0.70	0.49	0.46
10^2[H$_3$O$^+$]/M	1.50	2.00	3.00	5.00	10.0	
$10^2 k_{obs}$/s^{-1}	0.45	0.40	0.37	0.35	0.35	

(iii) Effect of hydrogen ion concentration when [Br$^-$] = 0.03M {10^4[KAu(CN)$_2$Br$_2$] = 8.1M; I = 0.21M}

10^2[H$_3$O$^+$]/M	0.00	0.50	6.40	10.0
10 k_{obs}/s^{-1}	0.70	0.65	0.76	0.70

(iv) Effect of concentration of (2) (10^2[H$_3$O$^+$] = 4.8M; [Br$^-$] = 0; I = 0.10M)

10^4[KAu(CN)$_2$Br$_2$]/M	3.5	23	35
$10^2 k_{obs}$/s^{-1}	0.30	0.33	0.36

(v) Effect of I {10^4[KAu(CN)$_2$Br$_2$] = 9.3M; 10^2[H$_3$O$^+$] = 9.6M, [Br$^-$] = 0}

I/M	0.10	0.20	0.30	0.50
$10^2 k_{obs}$/s^{-1}	0.34	0.33	0.33	0.32
I/M	0.70	0.90	1.10	
$10^2 k_{obs}$/s^{-1}	0.32	0.31	0.28	

(vi) Effect of temperature [10^4]KAu(CN)$_2$Br$_2$] = 6.5M; 10[Br$^-$] = 0.53M; [H$_3$O$^+$] = 0.08M}

T_p/°C	10.0	29.1	40.0
$10 k_{obs}$/s^{-1}	0.26	1.4	3.6

$\Delta H^{\ddagger}$ = 67 ± 2 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −56 + 5 J K^{-1} mol^{-1}

TABLE 2

Promotion by potassium tetrabromoaurate (1). [S-amide]$_{initial} \simeq 6.0 \times 10^{-5}$M; solvent 2% v/v ethanol-water, temperature = 25.0 °C, other symbols as Table 1

(i) Effect of bromide ion concentration {10^4[KAuBr$_4$] = 6.5M; I = 1.00M; 10^2[H$_3$O$^+$] = 0.94M}
See Figure 2

(ii) Effect of hydrogen ion concentration {10^4[KAuBr$_4$] = 6.9M; I = 1.00M; [Br$^-$] = 0.20M}

10^2[H$_3$O$^+$]/M	0.00	0.10	0.50
$10^2 k_{obs}$/s^{-1}	1.6	1.6	1.7
10^2[H$_3$O$^+$]/M	1.00	2.50	10.0
$10^2 k_{obs}$/s^{-1}	1.5	1.7	1.7

(iii) Effect of concentration of (1) {10^2[H$_3$O$^+$] = 9.4M; [Br$^-$] = 0.02M; I = 0.20M}

10^4[KAuBr$_4$]/M	4.9	9.8	24	39	49
$10^2 k_{obs}$/s^{-1}	1.1	1.0	0.76	0.72	0.74

that k_{obs} (i) is independent of the excess of concentration of (2), (ii) depends little upon ionic strength, (iii) is independent of [H$_3$O$^+$] at moderate ambient bromide ion concentrations, but is slightly dependent on [H$_3$O$^+$] (probably via a protonation equilibrium) at very low bromide

ion concentrations, and (iv) is increased markedly by increases in [Br$^-$] (Figure 1).

The u.v. spectrum of (2) in pure water has an absorption maximum at 324 nm (ϵ 900 ± 5). The equilibrium data of Ford-Smith et al.[4] indicate that negligible dis-
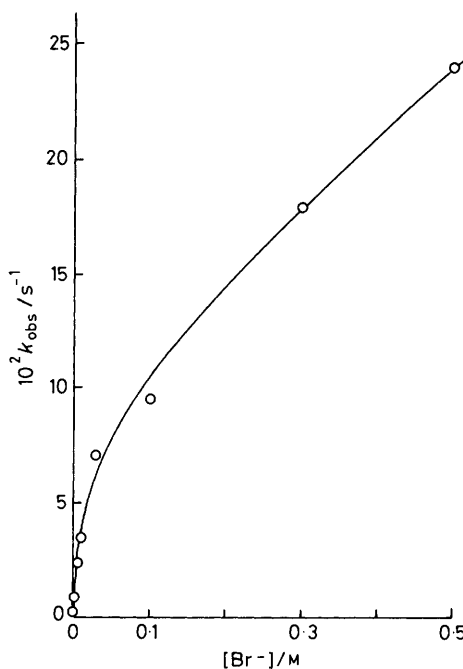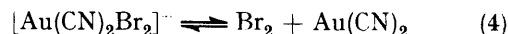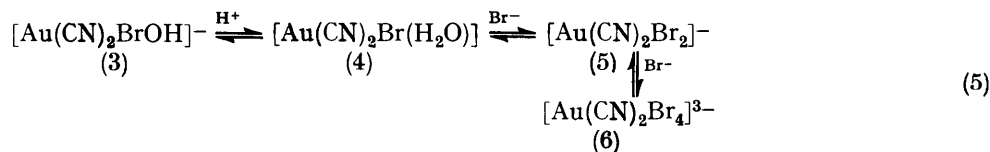

FIGURE 1   Effect of bromide ion concentration on promotion by (2). Conditions as in Table 1 (i)

sociation to gold(I) [equation (4)] occurs under these conditions.

$$[Au(CN)_2Br_2]^- \rightleftharpoons Br_2 + Au(CN)_2^- \qquad (4)$$

We find that the addition of bromide ions (as NaBr) leads to two effects: there occurs first a small increase in absorption at all wavelengths (complete when [Br$^-$] $\simeq$ 0.05M) followed by a more gradual, but much larger, increase in absorption at all wavelengths (still incomplete at [Br$^-$] 3.5M). At [Br$^-$] 0.1—0.2M, ϵ_{324} 957 ± 5; this value is in good agreement with Ford-Smith's value quoted for aqueous solutions containing an unspecified concentration of bromide ions. These observations suggest the occurrence of equilibria (5). Such equilibria are in keeping with the similar phenomena [1,2,6,7] which attend the addition of ambient halide ions to aqueous solutions of AuCl$_4^-$, [Au(dien)Cl]$^{2+}$, and AuBr$_4^-$ (see below). When [Br$^-$] $\simeq$ 0.05—0.20M the principal species in solution is likely to be (5). It is evident that species (7)—(10), analogous to (3)—(6), are likely to exist in solutions of the 1 : 1 adduct. We therefore suggest

$$[Au(CN)_2BrOH]^- \xrightarrow{\text{H}^+} [Au(CN)_2Br(H_2O)] \xrightarrow{\text{Br}^-} [Au(CN)_2Br_2]^-$$
$$(3) \qquad\qquad (4) \qquad\qquad (5) \downarrow \text{Br}^-$$
$$[Au(CN)_2Br_4]^{3-} \qquad\qquad\qquad (5)$$
$$(6)$$

the mechanism in Scheme 1 in explanation of our kinetic and other findings.

$$PhC\!\!\underset{NHR}{\overset{S}{\diagup}} + [Au(CN)_2Br_2]^- \underset{fast}{\rightleftharpoons}$$

$$[Ph\underset{|}{C}{=}S \rightarrow Au(CN)_2Br] + Br^- \quad (6)$$
$$\underset{NHR}{|} \quad (7)$$

$$(7) + H_2O \underset{fast}{\overset{K_7}{\rightleftharpoons}} [Ph\underset{|}{C}{=}S{\rightarrow}Au(CN)_2(H_2O)]^+ + Br^- \quad (7)$$
$$\underset{NHR}{|} \quad (8)$$

$$(8) + H_2O \underset{fast}{\overset{K_8}{\rightleftharpoons}} [Ph\underset{|}{C}{=}S{\rightarrow}Au(CN)_2OH] + H_3O^+ \quad (8)$$
$$\underset{NHR}{|} \quad (9)$$

$$(7) + 2Br^- \underset{fast}{\overset{K_9}{\rightleftharpoons}} [Ph\underset{|}{C}{=}S{\rightarrow}Au(CN)_2Br_3]^{2-} \quad (9)$$
$$\underset{NHR}{|} \quad (10)$$

$$(7) + 3H_2O \underset{slow}{\overset{k_{10}}{\longrightarrow}}$$
$$PhCONHR + [Au(CN)_2BrS]^{2-} + 2H_3O^+ \quad (10)$$

$$(8) + 3H_2O \underset{slow}{\overset{k_{11}}{\longrightarrow}}$$
$$PhCONHR + [Au(CN)_2(H_2O)S]^- + 2H_3O^+ \quad (11)$$

$$(9) + 3H_2O \underset{slow}{\overset{k_{12}}{\longrightarrow}}$$
$$PhCONHR + [Au(CN)_2(OH)S]^{2-} + 2H_3O^+ \quad (12)$$

$$(10) + 3H_2O \underset{slow}{\overset{k_{13}}{\longrightarrow}}$$
$$PhCONHR + [Au(CN)_2BrS]^{2-} + 2Br^- + 2H_3O^+ \quad (13)$$
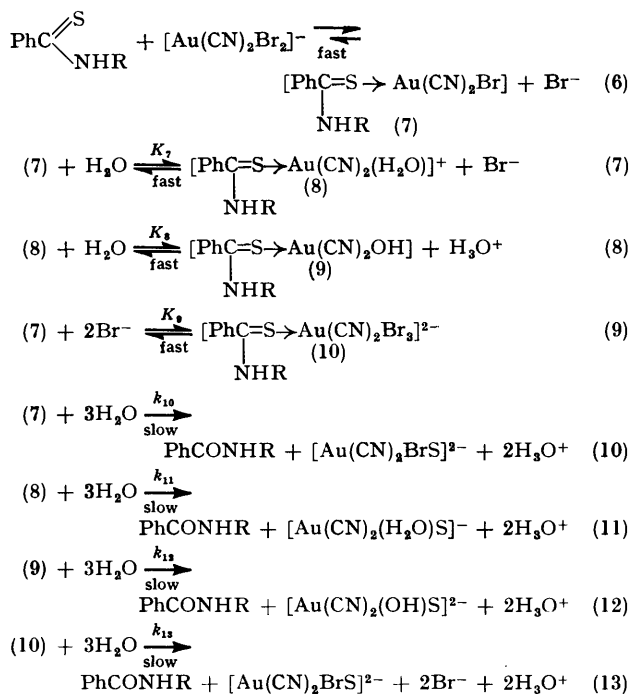
SCHEME 1

Scheme 1 leads to equation (14) for k_{obs}. This equation approximates to equation (15) at low bromide ion
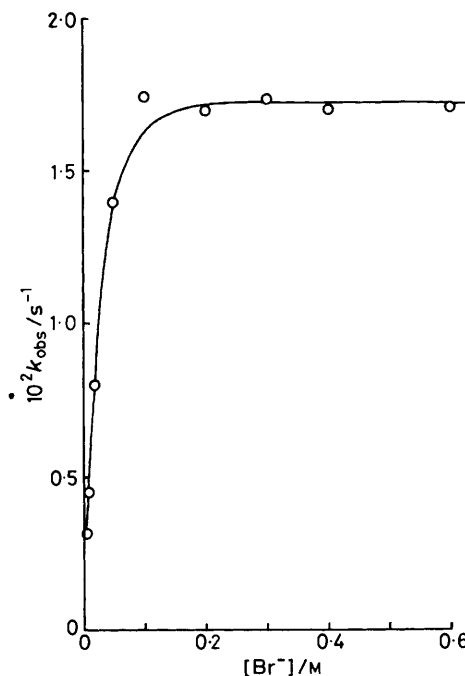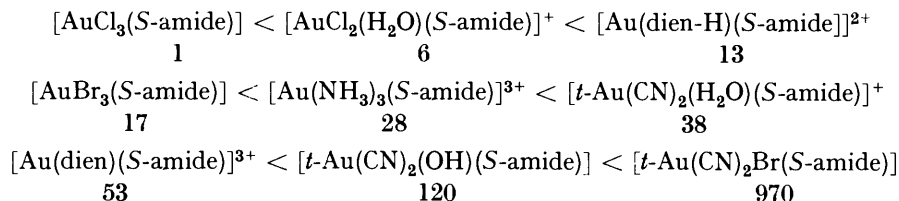

FIGURE 2 Effect of bromide ion concentration on promotion by (1). Conditions as in Table 2 (i)

383 nm (ϵ 4 600). At higher ambient bromide ion concentrations there occurs [7] a gradual but marked increase in absorption at all wavelengths (especially in the 300—330 nm region) which is still incomplete when [Br$^-$] 4.0M (by when $\epsilon_{max.} \simeq 5\,800$). As for AuCl$_4^-$ and

$$k_{obs} = \frac{k_{10}[H_3O^+][Br^-] + k_{11}K_7[H_3O^+] + k_{12}K_7K_8 + k_{13}K_9[H_3O^+][Br^-]^3}{[H_3O^+][Br^-] + K_7[H_3O^+] + K_7K_8 + K_9[H_3O^+][Br^-]^3} \quad (14)$$

concentrations. Plots of $1/k_{obs}$ against [H$_3$O$^+$] at low values of [H$_3$O$^+$] and of k_{obs} against $1/$[H$_3$O$^+$] at high values of [H$_3$O$^+$], using results in Table 1, lead to the values $k_{11} = 3.8 \times 10^{-3}$ s^{-1}, $k_{12} = 12 \times 10^{-3}$ s^{-1}, and

$$k_{obs} \simeq (k_{12}K_8 + k_{11}[H_3O^+])/(K_8 + [H_3O^+]) \quad (15)$$

$K_8 = 8.0 \times 10^{-4}$ mol dm^{-3}. These values, and the remaining kinetic data, permit the calculation of the other parameters. We find $k_{10} = 97 \times 10^{-3}$ s^{-1}, $k_{13} = 0.33$ s^{-1}, $K_7 = 12 \times 10^{-3}$ mol dm^{-3}, and $K_9 = 6.3$ mol^{-2} dm^6. Figure 1, in which the continuous line is computed from equation (14), shows that the suggested mechanism is compatible with the results. It is significant that changes in [H$_3$O$^+$] do not affect k_{obs} when [Br$^-$] > 0.03M; it is clear that under such conditions little formation of (8) and (9) occurs. This result is in keeping with the effect of bromide ions on the spectrum of (2) in the absence of S-amide (see above).

Promotion by Sodium Tetrabromoaurate (1).—Like the ions AuCl$_4^-$ and [Au(CN)$_2$Br$_2$]$^-$, AuBr$_4^-$ is known to undergo aquation in aqueous solutions at low ambient halide concentrations.[6] For AuBr$_4^-$, aquation is repressed when [Br$^-$] $\gtrsim$ 0.02M and in the region [Br$^-$] $\simeq$ 0.02— 0.1M the u.v. spectrum has a maximum absorption at *ca*.

Au(CN)$_2$Br$_2^-$, we attribute this effect to formation of octahedral species, here AuBr$_6^{3-}$. The spectral changes differ markedly from those [attributed to reduction to gold(I)] which have been observed [8] for acetonitrile solutions and Kazakov's work [9] shows in fact that negligible reduction occurs in aqueous solutions at the AuBr$_4^-$ and bromide ion concentrations used in the present study. As noted in the Experimental section, the S-amide–gold bromide adducts showed stoicheiometry greater than 2 : 1 at very low ambient bromide concentrations. This fact may be due to the aquation present under such conditions. To minimise aquation and to simplify interpretation we have therefore studied the promoted S-amide hydrolysis with [Br$^-$] > 0.005M.

Our kinetic results (Table 2, Figure 2) show that, for conditions of constant ionic strength, (i) k_{obs} increases sharply in the region [Br$^-$] = 5 $\times$ 10^{-3}—0.1M, but thereafter becomes independent of [Br$^-$], (ii) k_{obs} is independent of [H$_3$O$^+$] and (iii) k_{obs} decreases (slightly) to a constant value when [AuBr$_4^-$]$_{stoich}$ is made much greater than [S-amide]$_{initial}$. The results also suggest that changes in ionic strength have only a small effect on k_{obs}. We attribute the fall in k_{obs} when [AuBr$_4^-$] $\gg$ [S-amide]$_{initial}$ to the conversion of the 2 S-amide : 1
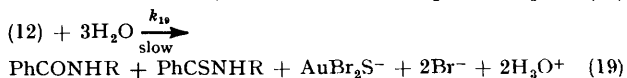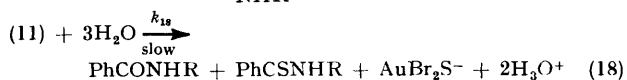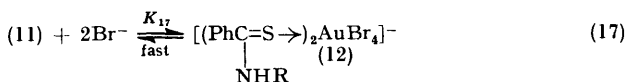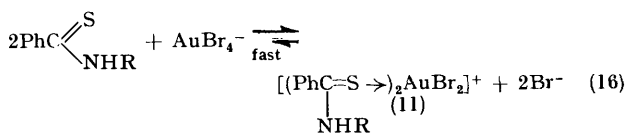
gold adducts, which exist when $[AuBr_4^-] \simeq [S$-amide], into 1 : 1-adducts. Most of our kinetic experiments were conducted with a *ca.* 10-fold excess of gold(III) ions; under such conditions both adducts probably co-exist with the 2 : 1 adduct predominating. The kinetic dependence on $[Br^-]$ is well accounted for by the mechanism of Scheme 2, which is analogous to that proposed for (2) at high bromide ion concentrations. Scheme 2 leads to equation (20) for k_{obs}. With $k_{18} = 3.3 \times 10^{-3}$

adducts are (7) and (10), is compatible with this suggestion.

Comparison with Previous Work.—Assuming, as an approximation, that the reactivity of $[PhC=S{\rightarrow}AuBr_3]$ is
$$\underset{NHR}{|}$$
about one half that of (11), the following approximate relative reactivities can be calculated for the square planar adducts at 25 °C:

$$[AuCl_3(S\text{-amide})] < [AuCl_2(H_2O)(S\text{-amide})]^+ < [Au(\text{dien-H})(S\text{-amide}]]^{2+}$$
$$1 \qquad\qquad 6 \qquad\qquad 13$$

$$[AuBr_3(S\text{-amide})] < [Au(NH_3)_3(S\text{-amide})]^{3+} < [t\text{-Au(CN)}_2(H_2O)(S\text{-amide})]^+$$
$$17 \qquad\qquad 28 \qquad\qquad 38$$

$$[Au(\text{dien})(S\text{-amide})]^{3+} < [t\text{-Au(CN)}_2(OH)(S\text{-amide})] < [t\text{-Au(CN)}_2Br(S\text{-amide})]$$
$$53 \qquad\qquad 120 \qquad\qquad 970$$

s^{-1}, $k_{19} = 16 \times 10^{-3}$ s^{-1}, and $K_{17} = 10^3$ mol^{-2} dm^6 this equation (Figure 2, continous line) well reproduces the k_{obs} values obtained experimentally. An equilibrium involving one bromide ion cannot match the data. The quantitative formation of the octahedral species when $[Br^-] \gtrsim 0.2M$ parallels the quantitative formation of the species $[PhC=S{\rightarrow}AuCl_5]^{2-}$ (13) in the $AuCl_4^-$-
$$\underset{NHR}{|}$$
promoted reaction.[1] In that system the formation of (13) was not complete until $[Cl^-] \gtrsim 2.0M$ (chloride ions are much harder ligands). The surprisingly great symbiotic effect of the resident (soft) S-amide ligand(s) on equlibria such as (17) is evident from the fact that, in the absence of the S-amide, these equilibria are not driven far to the right even at very high ambient halide ion concentrations (see above).

This sequence (which supercedes that in our preliminary report[10]) shows that (i) an increase in the positive charge on the gold atom and (ii) an increase in the softness of the attached ligands, are both factors which increase the rate of hydrolysis of the adduct. The softness effect appears to be the more important of these two factors. The powerful catalytic effect of iodide ions on similar reactions has already been noted.[11]

The octahedral species $[AuCl_5(S\text{-amide})]^{2-}$, $[Au(\text{dien-}H)Cl_2(S\text{-amide})]$, $[AuBr_5(S\text{-amide})]^{2-}$, $[Au(\text{dien})Cl_2(S\text{-amide})]^+$ and $[Au(CN)_2Br_3(S\text{-amide})]^{2-}$ are respectively *ca.* 30, 10, 5, 20, and 3 times more reactive than their square planar counterparts (which contain two less halide ions). There seems therefore to be a stronger attachment to the sulphur atom in the octahedral adducts in spite of their carrying two less positive charges. It is possible that the slow step of the sulphur abstraction reaction involves the reduction of the gold atom but there seems no doubt[6,8] that various gold(III) halides can form octahedral complexes in aqueous solution.[12]

$$2PhC\overset{\displaystyle S}{\underset{\displaystyle NHR}{\diagdown}} + AuBr_4^- \underset{fast}{\overset{}{\rightleftarrows}}$$

$$[(PhC{=}S\rightarrow)_2AuBr_2]^+ + 2Br^- \quad (16)$$
$$\underset{NHR}{\underset{|}{(11)}}$$

$$(11) + 2Br^- \underset{fast}{\overset{K_{17}}{\rightleftarrows}} [(PhC{=}S\rightarrow)_2AuBr_4]^- \quad (17)$$
$$\underset{NHR}{\underset{|}{(12)}}$$

$$(11) + 3H_2O \overset{k_{18}}{\underset{slow}{\longrightarrow}}$$
$$PhCONHR + PhCSNHR + AuBr_2S^- + 2H_3O^+ \quad (18)$$

$$(12) + 3H_2O \overset{k_{19}}{\underset{slow}{\longrightarrow}}$$
$$PhCONHR + PhCSNHR + AuBr_2S^- + 2Br^- + 2H_3O^+ \quad (19)$$

SCHEME 2

The slow steps written in Schemes 1 and 2 are doubtless not just single steps; moreover they will be followed

$$k_{obs} = (k_{18} + k_{19}K_{17}[Br^-]^2)/(1 + K_{17}[Br^-]^2) \quad (20)$$

by further transformations of the inorganic species. We suggest, however, in the light of earlier work,[1] that the slow processes involve attack by water on the carbonyl carbon atom of the co-ordinated S-amide. The value of $\Delta S^{\ddagger}$ for (2), which refers to conditions when the principal

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