

Effects of Ligands on the Gold(III)-promoted Hydrolysis of (*N*-Cyclohexyl)thiobenzamide

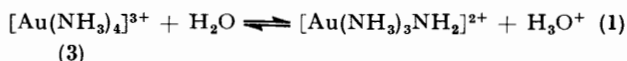
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A study is reported of the kinetics and mechanisms of the hydrolyses in aqueous solution at low pH of (*N*-cyclohexyl)thiobenzamide promoted by the ions $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ (1), $[\text{Au}(\text{dien-H})\text{Cl}]^+$ (2), $[\text{Au}(\text{NH}_3)_4]^{3+}$ (3), and $[\text{Au}(\text{phen})\text{Cl}_2]^+$ (4). Ions (1)–(3) employ mechanisms involving the relatively rapid displacement of Cl (or NH_3) by the *S*-amide, followed by slow hydrolysis steps; with (4) the slow substitution of the *S*-amide at gold probably controls the rate. The relative reactivities of the gold(III) species as promoters are given and the effects of changes in pH and in ambient chloride ion concentration on the reaction mechanisms are described.

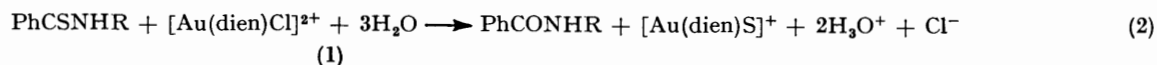
WE reported recently on the kinetics and mechanisms of the hydrolyses in aqueous solution of *N*-substituted *S*-benzamides¹ and of various *S*-esters^{2,3} promoted by the tetrachlorogold(III) ion. We give now details of the hydrolysis of (*N*-cyclohexyl)thiobenzamide to the corresponding *O*-amide promoted by the ions $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ (1), $[\text{Au}(\text{dien-H})\text{Cl}]^+$ (2), $[\text{Au}(\text{NH}_3)_4]^{3+}$ (3), and $[\text{Au}(\text{phen})\text{Cl}_2]^+$ (4) (where dien = diethylenetriamine and phen = 1,10-phenanthroline).

EXPERIMENTAL

Materials.—Diethylenetriaminechlorogold(III) dichloride was prepared by the method of Baddley *et al.*⁴ The product analysed correctly and its u.v. spectra in the 240–400 nm region obtained using aqueous solutions of different chloride ion concentration and pH agreed well with those reported by Baddley. At $\text{pH} \approx 5$ the chelating ligand loses a proton quantitatively to give solutions of (2). Tetra-ammine-gold(III) nitrate was prepared using a modification of Skibsted and Bjerrum's method.⁵ Tetrachloroauric acid was prepared from gold sponge (1 g) and dissolved in a solution of ammonium nitrate (95 g) in water (70 ml). Ammonia gas was passed through the resulting solution at 25 °C until the pH was stable at *ca.* 7.5. Standing (5 h) led to precipitation of a solid which was separated and dissolved in nitric acid (30 ml; $\text{pH} 2.0$ – 2.5) by warming to 35 °C (too high a temperature leads to discolouration). Filtration of the warm solution was followed by the addition of concentrated nitric acid (1.5 ml) and ethanol (30 ml) to the filtrate. Cooling to 0 °C led to a crystalline product (1.2 g, 50%). The product analysed correctly and its i.r. and u.v. spectra agreed with earlier reports.^{5,6} A determination of its $\text{p}K_a$ [reaction (1)], using NH_4ClO_4 – NH_3 buffers at ionic strength 1.0M, led to $\text{p}K_a 7.47 \pm 0.04$ at 25 °C, a value in excellent agreement with Skibsted's.⁵



Dichlorophenanthrolinegold(III) perchlorate was prepared by Harris's method⁷ (Found: C, 26.3; H, 1.6; N, 5.1; Cl, 19.3. Calc. for $\text{C}_{12}\text{H}_8\text{AuCl}_3\text{N}_2\text{O}_4$: C, 26.3; H, 1.5; N, 5.1; Cl, 19.4%). The compound had an absorption maximum at 280 nm with shoulders at 306 and 322 nm in aqueous solutions containing 0.8% (v/v) DMSO (or DMF). It can be



recrystallised without decomposition by dissolution in the minimum quantity of DMSO followed by a ten-fold dilution with water. (*N*-Cyclohexyl)thiobenzamide was a previous sample.¹ Water was doubly distilled and the other chemicals used in preparing reaction mixtures for kinetic work were the purest grades available commercially.

Kinetic Arrangements.—The hydrolyses [*e.g.* equation (2)] were followed by u.v. spectrophotometry (Unicam SP 1750 fitted with SP 1802 and SP 1805 accessories and thermostatted cell housing) along the lines used with tetrachlorogold(III) and other soft metal ions.^{1,8} Stock solutions of the *S*-benzamide were made in ethanol and all reaction mixtures contained 2–5% (v/v) ethanol; those for (4) usually also contained 2–4% (v/v) DMSO (or DMF) to retain (4) in solution throughout the reactions.

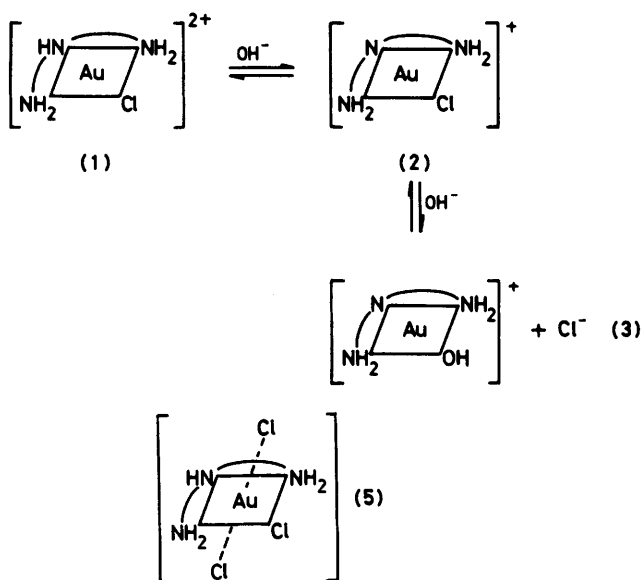
As for tetrachlorogold(III) ions, addition of an excess of (1)–(3) to the *S*-benzamide in aqueous solution leads to spectral changes which cannot be accounted for by the summation of the reactant spectra alone. In acid solution these changes are relatively rapid under the concentration conditions used (Tables) and precede the slower spectral changes which accompany the hydrolysis. The fast, initial changes represent adduct formation between the gold ions and the *S*-benzamide. Experiments using Harvey and Manning's method⁹ suggest that in all cases 1:1 adducts are formed quantitatively. With (4), however, initial spectral changes suggest that only a small quantity of a relatively highly absorbing adduct is formed whose spectrum is affected by the ambient hydrogen ion concentration. The spectral changes accompanying the hydrolysis of the adducts of (1)–(4) involve isosbestic points at 340, 304, 360, and 358 nm, respectively. During the hydrolyses a small amount of precipitation (presumably of a gold sulphide) sometimes occurs. This reduced the accuracy and reproducibility of some of the measurements with (4). After completion of the hydrolyses further slow precipitation was usual. Hydrolyses were always followed under pseudo-first-order conditions with the gold species normally in a ten or more-fold excess over the *S*-benzamide. The effects (Tables) of changes in the pH, in the gold and chloride (NaCl) concentrations, and in the temperature were all studied at constant ionic strength (NaClO_4). The observed first-order rate constant, k_{obs} , was computed from the absorbance (A_t) measurements using a program based on that of De Tar.¹⁰ Computed values of A_∞ were usually in good agreement with observed values; k_{obs} was normally

reproducible to within $\pm 20\%$ (often $\pm 10\%$) using different batches of reagents. Averages of two or more determinations are given in the Tables.

Reaction Products.—Preparative scale experiments, employing concentration conditions as similar as practicable to those of typical kinetic experiments, were conducted with each of the gold species (1)—(4). In all cases *N*-cyclohexylbenzamide was isolated in good yield as the only organic product. The complex gold sulphide, which is presumably formed as the initial inorganic product, probably undergoes further reactions since the final spectra show that more than one equivalent of gold is usually consumed.

RESULTS AND DISCUSSION

Aqueous Chemistry of the Gold Complexes.—Baddley's work^{4,11} shows (i) that, as the pH of an aqueous solution is raised above 2, (1) first loses a proton from the dien ligand to give (2) which subsequently undergoes replacement of the chloride ligand in the square plane by OH^- [equation (3)], (ii) that this chloride ligand in both (1) and (2) is readily replaced by bromide and other ions, and (iii) that in the presence of added chloride ions both (1) and (2) probably form octahedral chloro-complexes *e.g.*, (5). These processes all occur relatively rapidly. We



have confirmed these findings. The situation is slightly more complicated than described by Baddley in that the addition of neutral salts to aqueous solutions of (2) tends to reverse the N-H ionisation and so to reform (1). This also occurs when chloride salts are used, so that the effect of added chloride is two-fold: to produce octahedral species and to some extent to repress the N-H ionisation.

Skibsted's work⁵ with aqueous solutions of (3) shows that at acid pH it does not undergo N-H ionisation and is also stable to hydrolysis. Added bromide ions do, however, successively replace the NH_3 ligands in acid solution.¹² The known rates of these processes, and those^{11,18} of replacement of Cl^- by Br^- in (1) and (2) and in AuCl_4^- , considered together with the known¹⁴ rate of

substitution of (*N*-cyclohexyl)thiobenzamide into AuCl_4^- , indicate that the relatively rapid substitution of the *S*-benzamide into (1)—(3) is likely. This conclusion is in agreement with our findings concerning initial adduct formation (see Experimental section).

The spectra of (4) in various aqueous solutions containing 0.8% DMSO are in Figure 1. The strong absorp-

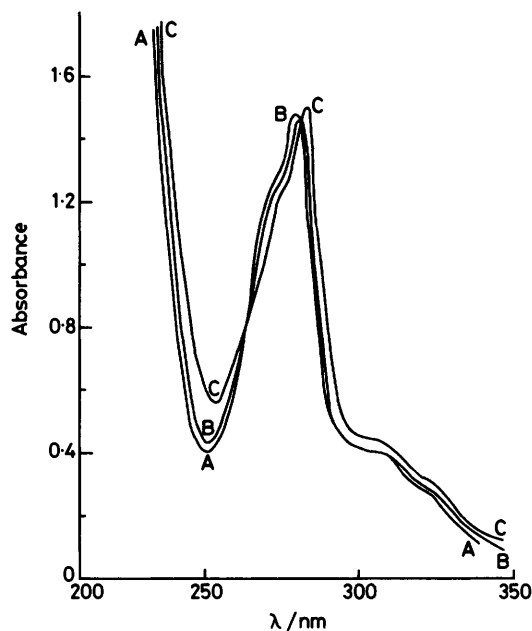
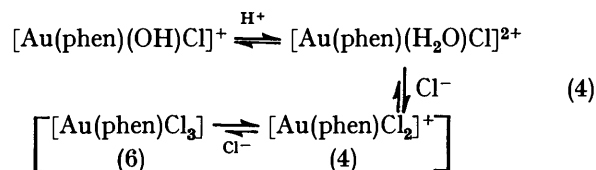


FIGURE 1 Spectra of dichlorophenanthrolinegold(III) perchlorate in various aqueous solvents. $[\text{Au}(\text{phen})\text{Cl}_2\text{ClO}_4] = 5.10 \times 10^{-6}\text{M}$. A, solvent only [0.8% (v/v) DMSO-water]; B, solvent with either 0.05M- HClO_4 or 0.10M- NaCl ; C, solvent with 4.3M- NaCl

tions at 280 nm and below are similar to those observed for free phenanthroline but are red-shifted by *ca.* 20 nm. As can be seen, they are largely unaffected by the presence of acid, in contrast to the effects found for free phenanthroline. The shoulder at 322 nm probably represents the characteristic gold absorption. Aqueous solutions of (4) are acidic⁷ and we have found that their pH can be raised by the addition of moderate concentrations (up to *ca.* 0.1M) of sodium chloride. However, little change in the u.v. spectrum results at these ambient chloride ion concentrations. At much higher chloride ion concentrations significant spectral changes do occur, especially in the 260–300 nm region. From experience with AuCl_4^- and other halogeno-gold(III) complexes,¹⁵ we attribute these changes to the acceptance by gold of apical chloride ions. Our observations as a whole suggest that DMSO does not readily displace the ligands in (4) and that the equilibria (4) occur in aqueous solutions. We



postulate a five-co-ordinate complex (6) in view of the similar species invoked by other workers.¹⁶ The lack of competition from DMSO is in agreement with findings¹⁷ for AuCl_4^- .

S-Benzamide Hydrolysis promoted by (1) and (2).—Our results are in Tables 1 and 2 and Figures 2–4. They

TABLE 1

Hydrolysis promoted by diethylenetriaminechlorogold(III) dichloride

$[\text{S-amide}]_{\text{init}} \approx 1.2 \times 10^{-4}\text{M}$; temperature 25.0 °C; solvent 5% (v/v) ethanol-water; ionic strength *I*

(i) Effect of Au^{III} concentration in absence of acid (*I* 0.30M)

| | | | | |
|--|------|------|------|------|
| $10^3[\text{Au}(\text{dien})\text{Cl}_2]/\text{M}$ | 0.77 | 1.53 | 2.30 | 2.95 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 7.1 | 7.1 | 7.5 | 7.1 |
| $10^3[\text{Au}(\text{dien})\text{Cl}_2]/\text{M}$ | 3.25 | | | |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 8.1 | | | |

(ii) Effect of Au^{III} concentration in presence of acid ($10^3[\text{H}_3\text{O}^+]$ 4.7M; *I* 0.30M)

| | | | | |
|--|------|------|------|------|
| $10^3[\text{Au}(\text{dien})\text{Cl}_2]/\text{M}$ | 0.66 | 1.31 | 1.77 | 2.93 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 3.3 | 3.7 | 3.3 | 3.7 |
| $10^3[\text{Au}(\text{dien})\text{Cl}_2]/\text{M}$ | 4.40 | | | |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 3.8 | | | |

(iii) Effect of ionic strength ($10^3[\text{H}_3\text{O}^+]$ 4.7M; $10^3[\text{Au}(\text{dien})\text{Cl}_2]$ 1.33M)

| | | | | |
|-------------------------------------|------|------|------|------|
| $10 I/\text{M}$ | 0.47 | 0.67 | 1.00 | 1.30 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 7.1 | 7.0 | 5.7 | 5.3 |
| $10 I/\text{M}$ | 1.80 | 2.30 | 3.50 | 4.00 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 5.0 | 4.1 | 3.8 | 3.3 |

(iv) Effect of chloride ion concentration in the absence of acid ($10^3[\text{Au}(\text{dien})\text{Cl}_2]$ 1.48M; *I* 0.60M)

| | | | | |
|-------------------------------------|------|------|------|------|
| $10[\text{NaCl}]/\text{M}$ | 0.00 | 0.25 | 0.50 | 0.75 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 1.8 | 5.0 | 8.1 | 10 |
| $10[\text{NaCl}]/\text{M}$ | 1.00 | 1.50 | 2.50 | |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 12 | 14 | 16 | |

(v) Effect of chloride ion concentration in presence of acid ($10^3[\text{Au}(\text{dien})\text{Cl}_2]$ 1.13M; *I* 0.80M; $10^3[\text{H}_3\text{O}^+]$ 4.7M)

| | | | | |
|-------------------------------------|------|------|------|------|
| $10[\text{NaCl}]/\text{M}$ | 0.00 | 0.05 | 0.10 | 0.50 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 3.3 | 5.0 | 5.8 | 11 |
| $10[\text{NaCl}]/\text{M}$ | 1.00 | 1.50 | 2.00 | |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 18 | 28 | 37 | |

TABLE 2

Effect of temperature on promotion by diethylenetriaminechlorogold(III) dichloride

$[\text{S-amide}]_{\text{init}} \approx 1.3 \times 10^{-4}\text{M}$; $[\text{Au}(\text{dien})\text{Cl}_2]$ $1.48 \times 10^{-3}\text{M}$; $[\text{H}_3\text{O}^+]$ $4.5 \times 10^{-2}\text{M}$; $[\text{NaCl}]$ 0.15M; solvent 4% (v/v) ethanol-water

| | | | |
|-------------------------------------|------|------|------|
| $T_p/\text{°C}$ | 8.5 | 18.8 | 27.0 |
| $10^3 k_{\text{obs}}/\text{s}^{-1}$ | 0.97 | 2.1 | 3.7 |

$$\Delta H^\ddagger 50 \pm 3 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger -110 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$$

show (i) that, at fixed ionic strength, an increase in $[\text{H}_3\text{O}^+]$ leads to an increase in k_{obs} (probably *via* a protonation equilibrium), (ii) that both at high and at low acid concentrations an increase in $[\text{Cl}^-]$ leads to a marked increase in k_{obs} , (iii) that an increase in the stoichiometric gold concentration has little effect in k_{obs} and that this small effect is largely accounted for by the concomitant increase in $[\text{Cl}^-]$ which arises because the gold complex is added as its dichloride (see Experimental section), and (iv) that an increase in ionic strength leads to a decrease in k_{obs} .

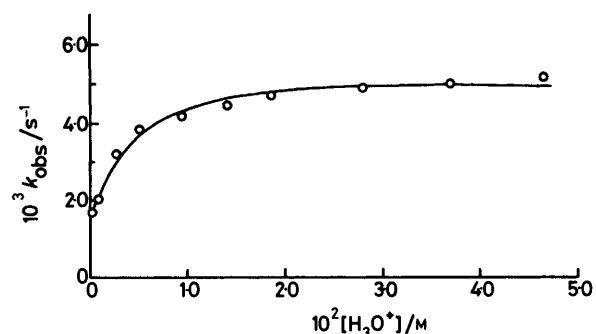


FIGURE 2 Effect of $[\text{H}_3\text{O}^+]$ on promotion by diethylenetriaminechlorogold(III) dichloride. $[\text{S-amide}]_{\text{init}} 1.23 \times 10^{-4}\text{M}$; $[\text{Au}(\text{dien})\text{Cl}_2]$ $1.34 \times 10^{-3}\text{M}$; *I* 0.10M; solvent 5% (v/v) ethanol-water; *T* 25.0 °C

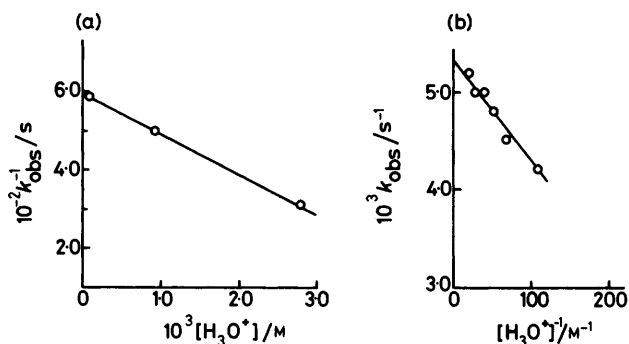


FIGURE 3 Promotion by diethylenetriaminechlorogold(III) dichloride. Conditions as for Figure 2. (a) Plot of $1/k_{\text{obs}}$ against $[\text{H}_3\text{O}^+]$; (b) Plot of k_{obs} against $1/[\text{H}_3\text{O}^+]$

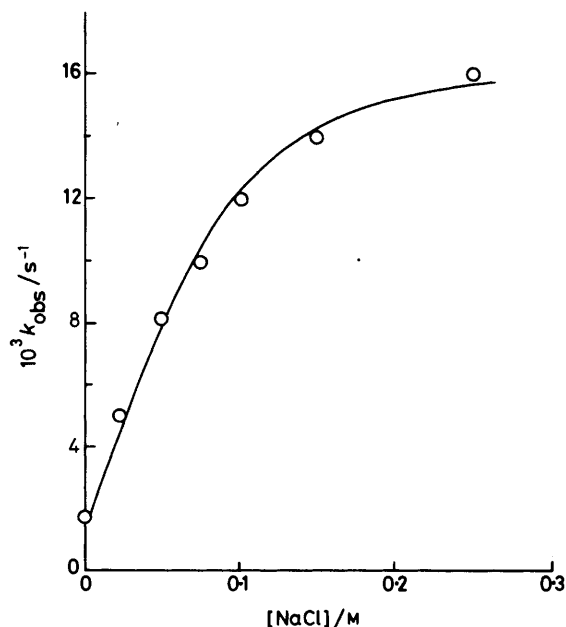
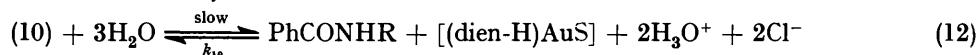
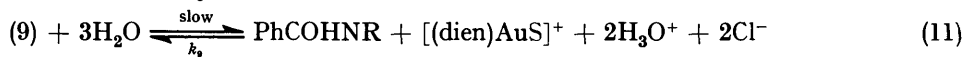
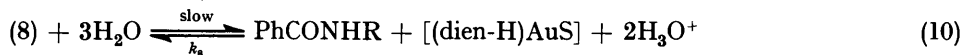
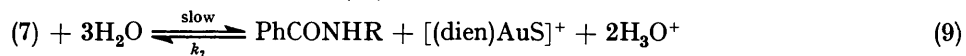
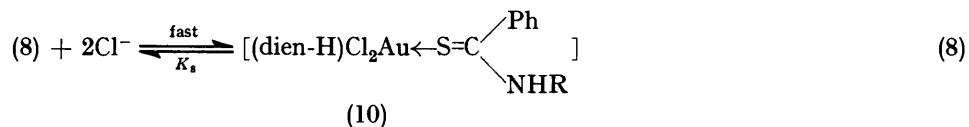
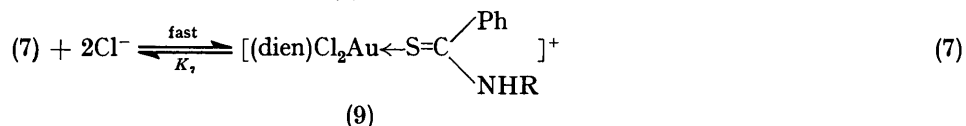
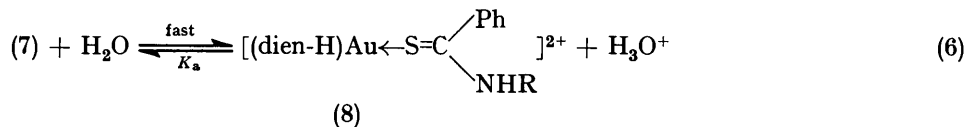
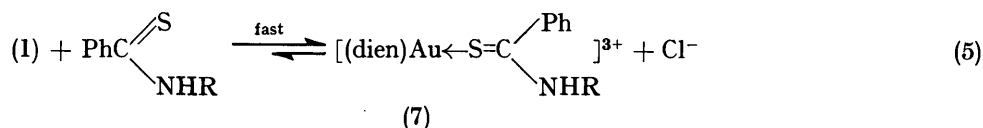


FIGURE 4 Effect of added chloride ions on the reactivity of (2). Conditions as in Table 1 (iv); continuous line calculated using equation (14)

In view of the known behaviour of (1) in aqueous solution and the observed rapid and stoichiometric 1:1 adduct formation with the *S*-benzamide, we suggest the mechanism in equations (5)–(12) for the promoted

hydrolysis. This scheme leads to rate equation (13) which gives equation (14) for k_{obs} , where the various

than those derived from (2). That is sensible in view of their respective charges. The relatively great reactivity



constants are defined by equations (5)–(12). In the absence of added chloride ions, equation (14) approx-

of the octahedral adducts is also in keeping with the results¹ for AuCl_4^- . Our value of K_a indicates that the

$$-d[1:1\text{-adduct}]_{\text{total}}/dt = k_7[(7)] + k_8[(8)] + k_9[(9)] + k_{10}[(10)] \\ = k_{\text{obs}}\{[(7)] + [(8)] + [(9)] + [(10)]\} \quad (13)$$

$$\therefore k_{\text{obs}} = \frac{k_7[\text{H}_3\text{O}^+] + K_a k_8 + K_7 k_9 [\text{H}_3\text{O}^+][\text{Cl}^-]^2 + K_a K_8 k_{10} [\text{Cl}^-]^2}{[\text{H}_3\text{O}^+] + K_a + K_7 [\text{H}_3\text{O}^+][\text{Cl}^-]^2 + K_a K_8 [\text{Cl}^-]^2} \quad (14)$$

imates to (15). At the extremes of high and low

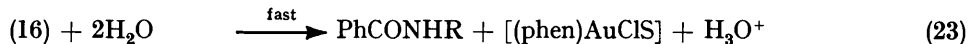
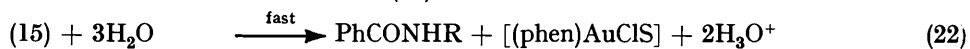
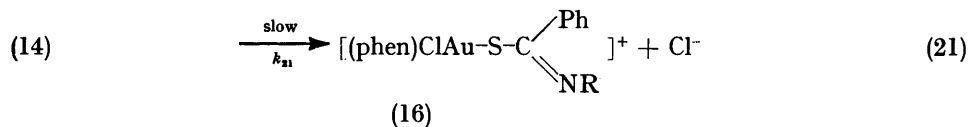
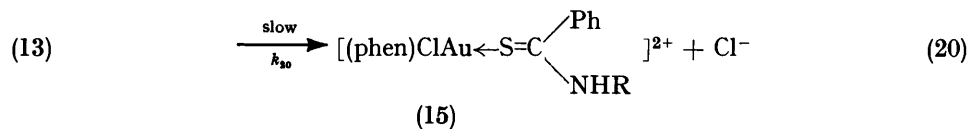
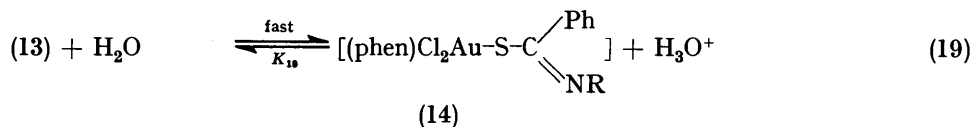
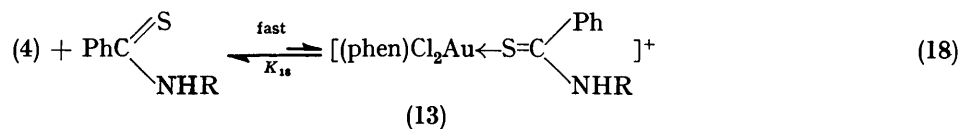
$$k_{\text{obs}} = K_a k_8 + k_7 [\text{H}_3\text{O}^+] / (K_a + [\text{H}_3\text{O}^+]) \quad (15)$$

hydrogen ion concentration equation (15) can be written as $k_{\text{obs}} = K_a k_8 / [\text{H}_3\text{O}^+] + k_7$ and $1/k_{\text{obs}} = 1/k_8 + [\text{H}_3\text{O}^+] / K_a k_8$, respectively. Plots of these equations (Figure 3) using data from Table 1 lead to values for k_7 , k_8 , and K_a . Equation (14) also simplifies under conditions of low hydrogen ion but high chloride ion concentration when values for K_8 and k_{10} can be obtained. Finally the data for intermediate concentrations can be used in conjunction with the constants already evaluated to obtain K_7 and k_9 . In this way we obtain k_7 $5.3 \times 10^{-3} \text{ s}^{-1}$, k_8 $1.6 \times 10^{-3} \text{ s}^{-1}$, k_9 0.14 s^{-1} , k_{10} $1.6 \times 10^{-2} \text{ s}^{-1}$, K_a $5.6 \times 10^{-3} \text{ mol dm}^{-3}$, K_7 $15 \text{ dm}^6 \text{ mol}^{-2}$, and K_8 $300 \text{ dm}^6 \text{ mol}^{-2}$. These values can be used to estimate k_{obs} for any combination of hydrogen and chloride ion concentrations, as illustrated by the continuous line in Figure 4. It is clear that the suggested mechanism is at least compatible with the kinetic data, as well as with the known chemistry of (1) and (2). Our values for the rate constants k_7 – k_{10} show that the adducts derived from (1) are more reactive

substitution of a neutral and very soft ligand for Cl^- *trans* to the ionising N–H group in (1) produces an increase in acidity. That too is an intelligible result. Perhaps surprising are our relative values of K_7 and K_8 .

The slow processes controlled by the constants k_7 – k_{10} almost certainly do not proceed in a single step as written in equations (9)–(12). The details of these slow processes are not known except that at low chloride ion concentration in the presence of acid an increase in ionic strength leads to a decrease in k_{obs} (Table 1). This result suggests that charge is lost or dispersed in the process controlled by k_7 . The entropy of activation (Table 2), which refers to conditions when mainly (7) and (9) are present in solution, suggests the involvement of water in the slow step. We suggest therefore that the slow steps probably all involve the attack of one or more water molecules on the thiocarbonyl carbon atom of the co-ordinated S-benzamide with concomitant opening of the C=S double bond, *e.g.* (11). Subsequent, faster steps are assumed to lead to the O-benzamide and other products.

S-Benzamide Hydrolysis promoted by (3).—Relatively



$$-d[\text{PhCSNHR}]/dt = k_{\text{obs}}[\text{PhCSNHR}] = k_{20}[(13)] + k_{21}[(14)] \quad (24)$$

$$k_{\text{obs}} = (K_{18}k_{20} + K_{18}K_{19}k_{21}/[\text{H}_3\text{O}^+])[(4)] \quad (25)$$

ably) independent of $[\text{Cl}^-]$. The runs in the presence of added chloride ions were accompanied by precipitation and k_{obs} was difficult to obtain reliably.

In the light of the known tendency of phenanthroline-gold derivatives to give a five-co-ordinate species,¹⁶ we

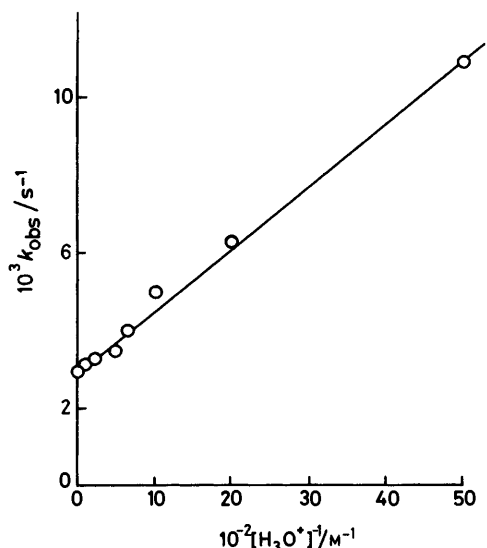


FIGURE 6 Plot of equation (25). Conditions as for Figure 5

tentatively suggest the outline mechanism of equations (18)—(23) for the promoted hydrolysis. This mechanism leads to rate equation (24) and k_{obs} is given by equation (25). This equation is in agreement with the observed first-order dependence on gold concentration and the probable lack of dependence on $[\text{Cl}^-]$. A plot (Figure 6) of k_{obs} against $1/[\text{H}_3\text{O}^+]$, for conditions of fixed ionic

strength and gold concentration, shows that the proposed mechanism is also compatible with the data in Figure 5. This is the first occasion we have had to postulate N-H ionisation from the S-amide in gold(III) ion promotion. The pH region involved is, however, similar to those involved for this type of ionisation in the analogous Hg^{II} , Ag , and Cu^{II} systems.⁸

As written, the slow steps represent square planar substitutions from five-co-ordinate species. It may be that the hydrolysis steps (22) and (23) occur synchronously with (20) and (21). Since steps (20) and (21) involve the creation of charges, the increase in k_{obs} with ionic strength (Table 5) would be expected. Whatever the exact mechanism it is evident that co-ordination of the S-benzamide to (4) results in a relatively rapid promotion of hydrolysis.

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REFERENCES

- A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1351.
- A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1278.
- G. Patel, R. S. Satchell, and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1406.
- W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poe, *Inorg. Chem.*, 1963, 2, 921.
- L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand.*, 1974, **A28**, 740.
- M. Weishaupt and J. Strahle, *Z. Naturforsch.*, 1976, **31B**, 554.
- C. M. Harris, *J. Chem. Soc.*, 1959, 682.
- A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1366 and earlier papers.
- A. E. Harvey and D. Manning, *J. Am. Chem. Soc.*, 1950, **72**, 4488.
- D. F. De Tar in 'Computer Programs for Chemistry,' ed. D. F. De Tar, Benjamin, New York, 1968, vol. 1, p. 117.
- W. H. Baddley and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1087.
- L. H. Skibsted, *Acta Chem. Scand.*, 1979, **A33**, 113.

¹³ L. I. Elding and A. B. Gröning, *Acta Chem. Scand.*, 1978, **A32**, 867.

¹⁴ A. J. Hall and D. P. N. Satchell, *Chem. Ind. (London)*, 1976, 373.

¹⁵ J. V. Micallef, Thesis, University of London, 1982.

¹⁶ R. J. Puddephatt, 'The Chemistry of Gold,' Elsevier, Amsterdam, 1978.

¹⁷ R. A. Potts, *Inorg. Chem.*, 1970, **9**, 1284.