Hydrolysis of *N*-Cyclohexyl Methylthiobenzimidate in the Presence of Tetrachlorogold(III) Ions and the Effects of Hydrogen, Halide, and Other Ions

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In aqueous acid the hydrolysis of *N*-cyclohexyl methylthiobenzimidate is promoted by tetrachlorogold(III) ions, and ions derived therefrom. A kinetic study shows that the reaction involves the rapid co-ordination of a small fraction of the free thiobenzimidate ester. or of its protonated form. to the species [AuCl$_3$OH]$^-$. [AuCl$_3$H$_2$O], [AuCl$_4$]$^-$, and [AuCl$_6$]$^{3-}$ by displacement of chloride. The slow step is the decomposition of the resulting gold–ester complex either unimolecularly (where possible) or *via* attack by water. The principal complexes involved under given conditions depend upon the values of [H$_3$O$^+$] and [Cl$^-$]. All these effects are described. The purely organic product is always *N*-cyclohexylbenzamide. The other product(s) is a complex organogold sulphide whose exact composition probably depends upon the inorganic content of the reaction mixture. Normally two equivalents of gold are consumed per equivalent of ester. In the presence of iodide ions catalysis of the gold-promoted hydrolysis is found. This arises from the relatively rapid formation of mixed chloroiodogold(III) complexes (*e.g.* [AuCl$_3$I]$^-$) which co-ordinate a greater fraction of the ester and thus accelerate its hydrolysis. The detailed effects of hydrogen and chloride ion concentrations on the iodide catalysed reaction are described. Of other soft bases tested as catalysts, bromide ion is moderately effective. but cyanide and thiocyanate ions, although they enter the gold(III) complexes. lead to species which provide no catalysis of thiobenzimidate ester hydrolysis.

WE reported recently on the reactions of thiobenzimidate esters with water in the presence of hydrogen ions and of mercury(II) ions.[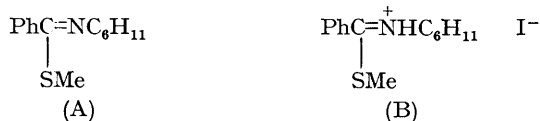1] We have extended this work to reactions in the presence of tetrachlorogold(III) ions. There appears to be no previous work on this topic.

[1] A. J. Hall and D. P. N. Satchell, preceding paper.

EXPERIMENTAL

Materials.—N-Cyclohexyl methylthiobenzimidate (A), its hydrogen iodide (B), and N-cyclohexylbenzamide were previous samples.[1] Potassium cyanide, bromide, iodide, and thiocyanate were the purest available commercial materials. The sources of the remaining chemicals were the same as in our previous work.
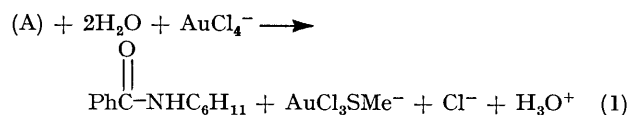
Tests for Complex Formation.—Certain sulphur-containing compounds form complexes quantitatively with tetrachlorogold(III) ions in aqueous solution.[2] In the present system spectroscopic tests showed that any similar complexes formed between the gold compounds and (A) must be formed in very low concentrations.

$$\underset{\underset{\text{(A)}}{\underset{|}{\text{SMe}}}}{\text{PhC=NC}_6\text{H}_{11}} \qquad \underset{\underset{\text{(B)}}{\underset{|}{\text{SMe}}}}{\overset{+}{\text{PhC=NHC}_6\text{H}_{11}}} \quad \text{I}^-$$

Kinetic Arrangements.—These followed the previous pattern. The solvent was 2% v/v ethanol–water. Loss of thiobenzimidate ester was normally followed at 260 nm. In some runs reaction was initiated by the addition of (A), in others, where the effects of iodide ions were being studied, by the addition of (B). Certain reaction mixtures were deliberately aged for 24 h before initiation, but most mixtures were allowed 15 min to reach the required temperature in the thermostatted housing of the Unicam SP 800 spectrophotometer. In some mixtures containing iodide ion, at low gold and chloride ion concentrations, precipitation of solid was evident soon after the start of a run. All other reaction mixtures remained homogeneous throughout. Hydrolyses in the absence of iodide ions exhibited an accurately first-order loss of ester when the gold species were present in a sufficient ($\geqslant$10-fold) excess. Such an excess was sometimes inconvenient spectroscopically and the majority of the runs were conducted using a six-fold excess, measurements being then restricted to the first half-life of the hydrolysis. The observed first-order rate constant, k_{obs}, was calculated from a plot of $\log (D - D_\infty)$ against time. Values of k_{obs} were reproducible to within $\pm 10\%$. Variation of the initial ester concentration confirmed that the order in ester was indeed unity in the absence of iodide. In the presence of iodide ions at concentrations equivalent to, or similar to, that of the ester, the observed loss of ester was found to be a second-order process, iodide being also consumed. The observed second-order constant, k_2, was calculated from plots of the appropriate second-order rate equation, in most cases from $ak_2t = x/(a - x)$, where x represents the amount of reaction at time t and a is the initial concentration of (B) (which contains ester and iodide in equivalent amounts). Values of k_2 were reproducible to within $\pm 10\%$. High iodide ion concentrations were avoided since[3] they can lead to reduction of Au^{III} to Au^{I}. No such reduction was detectable in our experiments at low iodide concentrations (see also Discussion section). Bromide ions can be used in high concentrations without risk of any such reduction and the catalysed loss of ester in the presence of a $\geqslant$10-fold excess of bromide ions is a (pseudo)-first-order process (k_{obs}). Our results for k_{obs} and k_2 for various concentrations of gold(III), hydrogen, halide, and other ions, and for conditions of both constant and variable ionic strength, are in Tables 1 and 2.

Products.—Preparative scale experiments, which simu-

lated as far as possible the concentration conditions of the kinetic runs, showed that under all conditions the purely organic product is N-cyclohexylbenzamide which is formed in high yield. The spectra of reaction mixtures left for >10 half-lives are also compatible with this conclusion. The gold compound therefore effects the removal of the SMe group and its replacement by oxygen. The inorganic products will obviously depend upon the exact inorganic composition of the reaction mixture and are unknown, but it is evident from the changes in the spectrum of AuCl$_4^-$ in reaction mixtures that two equivalents of gold(III) ions are consumed per equivalent of thiobenzimidate ester. The initial overall reaction is perhaps (1) (see also Discussion section) which will be followed by further transformation of the gold species. In the presence of iodide and of other inorganic anions various gold(III) complexes can obviously form (see Discussion section).

$$\text{(A)} + 2\text{H}_2\text{O} + \text{AuCl}_4^- \longrightarrow$$
$$\underset{\underset{\text{PhC-NHC}_6\text{H}_{11}}{\|}}{\text{O}} + \text{AuCl}_3\text{SMe}^- + \text{Cl}^- + \text{H}_3\text{O}^+ \quad (1)$$

RESULTS AND DISCUSSION

Experiments with the Free Ester (A).—Typical results are in Table 1. The velocity of hydrolysis of (A) [or

TABLE 1

Experiments with N-cyclohexyl methylthiobenzimidate (A)

[Ester]$_{initial}$ *ca.* 5×10^{-5}M (except as stated); temperature 23°; solvent 2% v/v ethanol–water

Effect of [AuCl$_4^-$]

(i) [Cl$^-$] = 0, 10^3[H$_3$O$^+$] = 1.82M

10^4[AuCl$_4^-$]/M	2.5	3.0	3.5	4.0	
$10^4 k_{obs}$/s^{-1}	1.82	2.15	2.58	2.88 (2.80) *	

(ii) [Cl$^-$] = 0.04M, 10^3[H$_3$O$^+$] = 1.82M

10^4[AuCl$_4^-$]/M	2.5	3.0	3.5	4.0
$10^4 k_{obs}$/s^{-1}	0.22	0.25	0.28	0.32 (0.33) *

Effect of [Cl$^-$] (10^3[H$_3$O$^+$] = 1.82M; 10^4[AuCl$_4^-$] = 3.0M)

10^3[Cl$^-$]/M	0.0	0.04	0.40	0.80	2.0	4.0
$10^4 k_{obs}$/s^{-1}	2.15	2.06	1.97	2.12	1.99	1.65

10^3[Cl$^-$]/M	6.0	10.0				
$10^4 k_{obs}$/s^{-1}	0.65	0.46				

10^2[Cl$^-$]/M	2.0	4.0	6.0	8.0	10.0	16
$10^4 k_{obs}$/s^{-1}	0.33	0.25	0.22	0.15	0.39 †	0.085

10^2[Cl$^-$]/M	32	64
$10^4 k_{obs}$/s^{-1}	0.054	0.031

10^2[Cl$^-$]/M	200	200
$10^4 k_{obs}$/s^{-1}	0.022	0.044 †

Effect of [H$_3$O$^+$]

(i) [Cl$^-$] = 0.04M, 10^4[AuCl$_4^-$] = 3.0M

10^3[H$_3$O$^+$]/M	1.00	2.73	3.64	5.46	7.28	9.12
$10^4 k_{obs}$/s^{-1}	0.34	0.14	0.12	0.10	0.077	0.062

10^3[H$_3$O$^+$]/M	90.0	450
$10^4 k_{obs}$/s^{-1}	0.040	0.038

(ii) [Cl$^-$] = 0, 10^4[AuCl$_4^-$] = 3.0M

10^3[H$_3$O$^+$]/M	1.00	1.82	9.12	18.2	90.0	450
$10^4 k_{obs}$/s^{-1}	2.26	2.15	2.20	1.54	1.10	0.81

* [Ester] = 2.5×10^{-5}M
† In the presence of 3.0×10^{-4}M-Br$^-$.

[2] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 1351.
[3] A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, 1961, **35**, 2206.

(B)] in aqueous acid solution in the absence of gold species [1] is relatively slow and, at pH $\gtrsim 3$, decreases as [H_3O^+] rises. The rates now observed in the presence of gold species are always $\geqslant 10$-fold faster than those

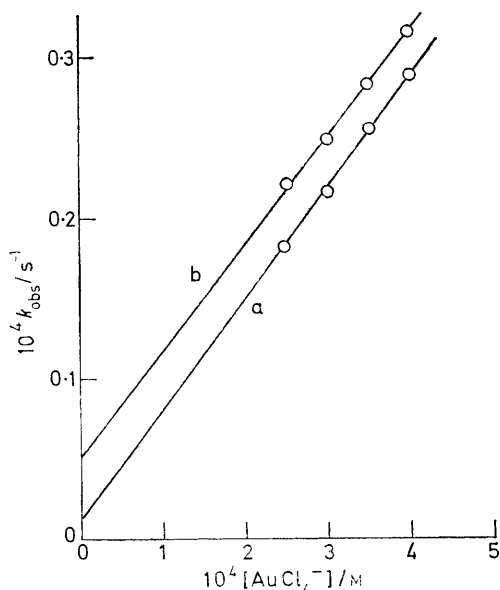FIGURE 1   Reaction order in $AuCl_4^-$: a, [Cl^-] = 0; b, [Cl^-] = 0.04M

found in the absence of gold, except at very high chloride and at low gold concentrations when the rates approach those found in the absence of gold species.[1] Our results lead to the following conclusions.

(i) At fixed chloride and hydrogen ion concentrations, the gold-promoted hydrolysis is first-order in [$AuCl_4^-$]$_{stoich}$. (The intercepts at [$AuCl_4^-$]$_{stoich}$ = 0 in Figure 1 are compatible with the expected rates of hydrolysis in the presence of the other components alone.[1])

(ii) An increase in chloride ion concentration, at fixed values of [$AuCl_4^-$] and [H_3O^+], leads to an eventual systematic decrease in k_{obs}. (Similar patterns of chloride ion effects are found for variable and for constant ionic strength—see below.) This fall in k_{obs} begins (Table 1) when [Cl^-] $\gtrsim 10^{-3}$M, which is the point at which significant amounts of the aquo-species [$AuCl_3H_2O$] and [$AuCl_3OH$]$^-$, known [4] to be present at low chloride ion concentrations, begin to be converted into [$AuCl_4$]$^-$.

(iii) The effect of an increase in [H_3O^+], at fixed values of [Cl^-] and [$AuCl_4^-$]$_{stoich}$, depends upon the value of [Cl^-] involved. At moderate (and high) chloride ion concentrations increasing acidity leads to a systematic fall in k_{obs}, whereas when [Cl^-] = 0 a more gradual and smaller decrease in k_{obs} is found for a large change in [H_3O^+].

The foregoing results, the known [2,4] equilibria in-

[4] P. van Z. Bekker and W. Robb, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 849; B. I. Peschevitskii, V. I. Belevantsev, and N. V. Kurbatova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1007.

volving [$AuCl_4$]$^-$, the known [5] extent of N-protonation of benzimidate esters in aqueous acid, and the fact that no appreciable amount of the ester is converted to gold–ester complexes, together with our previous conclusions about other metal-promoted hydrolyses,[1,2,6] lead us to suggest processes (2)—(5) for the present reaction. The equilibria in equations (2) and (3) are all assumed to be established rapidly. Other equilibria interconnecting the various species are, of course, possible but need not be specified explicitly. It is assumed that all the species (1)—(8) can undergo slow decomposition leading to the products as for example does (7) in equations (4) and (5). Any subsequent reactions of the gold complex are taken to be fast. Processes (2)—(5) are somewhat elaborate, but not over-elaborate in view of known equilibria and the present experimental facts. The latter can be seen to be accounted for as follows.

(i) The observed reaction order in gold is expected since all the reactive gold–ester complexes (1)—(8) involve only one atom of gold and are formed in low concentrations relative to the ester-free gold complexes.

(ii) If the reactivities towards hydrolysis of the various gold–ester complexes are not very different, or if one dominates, a progressive fall in k_{obs} would be expected as [Cl^-] rises owing to the displacement of ester by chloride ions. Indeed then k_{obs} should be inversely proportional to [Cl^-], since only a small fraction of the ester is complexed. It may be that species such as (4) and (8), which play such an important role in the
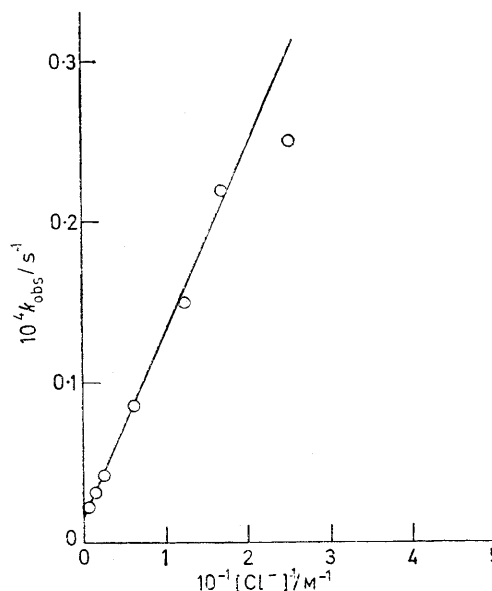

FIGURE 2   Effect of chloride ions in the absence of iodide ions

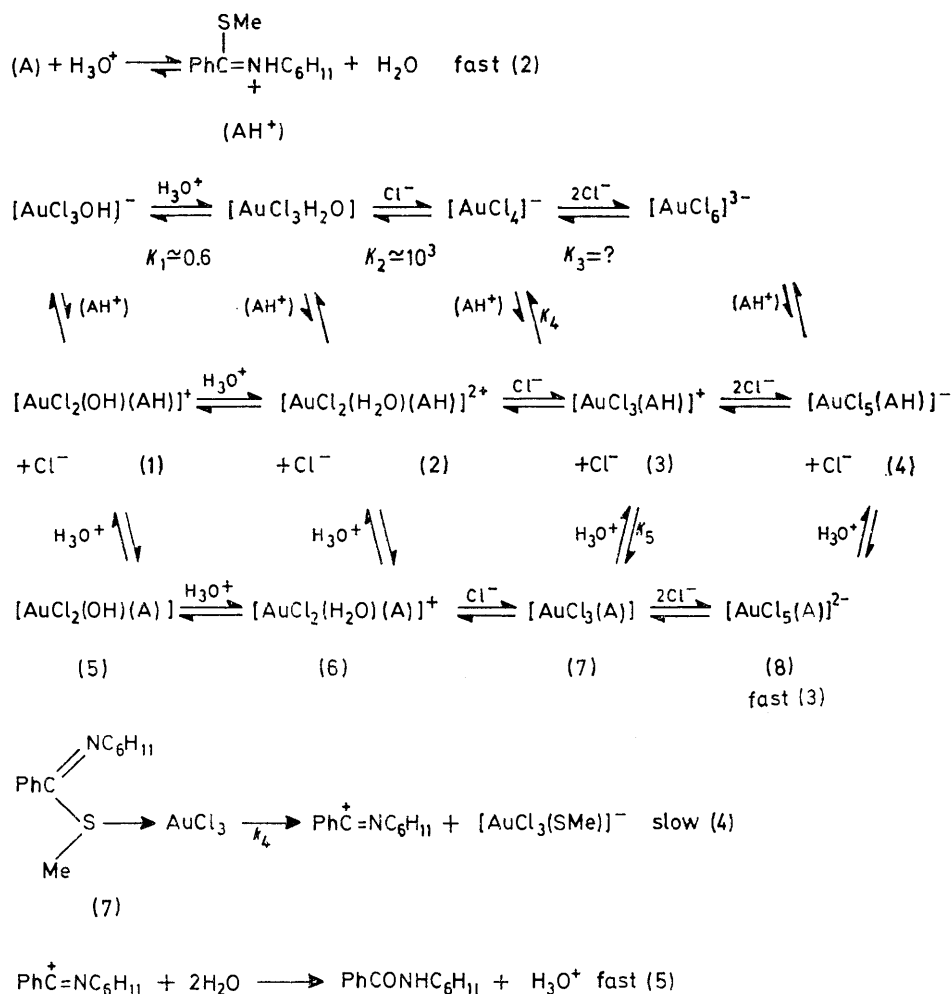gold-promoted hydrolysis of thioamides,[2] are relatively unimportant with the weakly complexing thiobenzimidate esters [1] which perhaps do not displace chloride ions significantly from [$AuCl_6$]$^{3-}$ at the high chloride ion

[5] R. K. Chaturvedi, A. E. MacMahon, and G. L. Schmir, *J. Amer. Chem. Soc.*, 1967, **89**, 6984.

[6] See also A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778, 953, 1273.
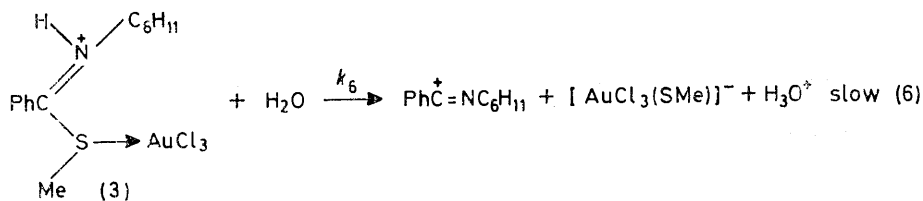
concentration at which $[AuCl_6]^{3-}$ probably exists.[2,7] In fact when $[Cl^-] \gtrsim 0.04M$, at which concentrations $[AuCl_4]^-$ and any $[AuCl_6]^{3-}$ dominate the other ester-free gold species, k_{obs} is indeed inversely proportional to

and (8) are more reactive than (3) and (4), respectively. This is likely: the separation of the gold complex will be expected to be easier from (7) [equation (4)] than from (3) where simultaneous removal of the extra proton

$$(A) + H_3O^+ \rightleftharpoons Ph\overset{\overset{\displaystyle SMe}{|}}{C}=NHC_6H_{11} + H_2O \quad fast \ (2)$$
$$(AH^+)$$

$$[AuCl_3OH]^- \underset{K_1 \simeq 0.6}{\overset{H_3O^+}{\rightleftharpoons}} [AuCl_3H_2O] \underset{K_2 \simeq 10^3}{\overset{Cl^-}{\rightleftharpoons}} [AuCl_4]^- \underset{K_3 = ?}{\overset{2Cl^-}{\rightleftharpoons}} [AuCl_6]^{3-}$$

$$\downarrow (AH^+) \qquad (AH^+) \downarrow \qquad (AH^+) \downarrow K_4 \qquad (AH^+) \downarrow$$

$$[AuCl_2(OH)(AH)]^+ \overset{H_3O^+}{\rightleftharpoons} [AuCl_2(H_2O)(AH)]^{2+} \overset{Cl^-}{\rightleftharpoons} [AuCl_3(AH)]^+ \overset{2Cl^-}{\rightleftharpoons} [AuCl_5(AH)]^-$$

$$+Cl^- \quad (1) \qquad +Cl^- \quad (2) \qquad +Cl^- \quad (3) \qquad +Cl^- \quad (4)$$

$$H_3O^+ \downarrow \qquad H_3O^+ \downarrow \qquad H_3O^+ \Big/ k_5 \qquad H_3O^+ \Big/$$

$$[AuCl_2(OH)(A)] \overset{H_3O^+}{\rightleftharpoons} [AuCl_2(H_2O)(A)]^+ \overset{Cl^-}{\rightleftharpoons} [AuCl_3(A)] \overset{2Cl^-}{\rightleftharpoons} [AuCl_5(A)]^{2-}$$

$$(5) \qquad\qquad (6) \qquad\qquad (7) \qquad\qquad (8)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad fast \ (3)$$

$$Ph\overset{NC_6H_{11}}{\underset{\overset{\displaystyle |}{\underset{\displaystyle Me}{S}}}{C}} \longrightarrow AuCl_3 \xrightarrow{k_4} Ph\overset{+}{C}=NC_6H_{11} + [AuCl_3(SMe)]^- \quad slow \ (4)$$
$$(7)$$

$$Ph\overset{+}{C}=NC_6H_{11} + 2H_2O \longrightarrow PhCONHC_6H_{11} + H_3O^+ \quad fast \ (5)$$

[Cl⁻] (see Figure 2), in keeping with this line of argument. At lower chloride ion concentrations, and at the hydrogen ion concentrations used, $[AuCl_4]^-$ is progressively replaced by $[AuCl_3(OH)]^-$. If therefore (1) and (5) are less reactive than are (3) and (7) the two

by a water molecule will be required [equation (6)]. A similar situation applies for the pair (8) and (4). When $[Cl^-] \simeq 0.04$—$0.1M$ the principal gold species will be $[AuCl_4]^-$. The proposed reaction scheme then approximates to just the third vertical column of equation (3)

$$Ph\overset{\overset{\displaystyle H}{\underset{\displaystyle \Vert}{\underset{\overset{\displaystyle +}{N}}{}}}{\underset{\overset{\displaystyle |}{\underset{\displaystyle Me}{S} \longrightarrow AuCl_3}}{C}} \ \overset{C_6H_{11}}{} + H_2O \xrightarrow{k_6} Ph\overset{+}{C}=NC_6H_{11} + [AuCl_3(SMe)]^- + H_3O^+ \quad slow \ (6)$$
$$(3)$$

effects of changing chloride ion concentration are opposing each other and k_{obs} should become less dependent on [Cl⁻] as found.

(iii) The fall in k_{obs} as $[H_3O^+]$ is increased at high or moderate values of [Cl⁻] is expected if complexes (7)

together with equations (4) and (6), so far as the kinetically relevant steps are concerned. For fixed values of [Cl⁻] and $[AuCl_4^-]$ this simplified scheme leads to the

[7] G. Annibale, L. Cattalini, A. A. El-Awady, and G. Natile, J.C.S. Dalton, 1974, 802.

rate equation (7), the constants being defined by equations (3), (4), and (6). A plot (Figure 3) of the relevant results in Table 1 leads to a good straight line
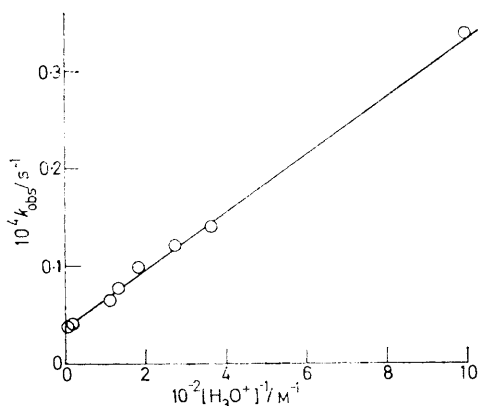

FIGURE 3 Plot of equation (7)

from which can be calculated $k'_6 = 3.8 \times 10^{-6}$ s^{-1} and $k'_4 = 2.9 \times 10^{-8}$ mol l^{-1} s^{-1}.

$$-\frac{1}{[\text{Ester}]}\frac{\text{d}[\text{Ester}]}{\text{d}t} = k_{\text{obs}}$$

$$= (k_6 K_4 + k_4 K_4 K_5/[\text{H}]\quad \frac{[\text{AuCl}_4^-]}{[\text{Cl}^-]}$$

or $\quad k_{\text{obs}} = k'_6 + k'_4/[\text{H}_3\text{O}^+]$ \qquad (7)

(iv) When [Cl$^-$] = 0 the fact that changes in [H$_3$O$^+$] have relatively little effect on k_{obs} suggests that the expected decrease in velocity arising from protonation of the co-ordinated ester is nearly offset by an increase in rate due to some other effect. This increase probably arises from the conversion of (1) and (5) to (2) and (6) respectively, for the greater the positive charge carried by the gold part of the complex the more easily will that part be able to leave with the SMe$^-$ group. We conclude therefore that the reactivities of the different gold–ester complexes in reactions (4) and (6) are (5) < (6) > (7) and (1) < (2) > (3), respectively. In the gold-promoted hydrolysis of thioamides [2] complexes like (5) and (6) have roughly equal reactivities, but a different type of rate-determining step is involved in that reaction.

Experiments with the Hydrogen Iodide (B).—If the thiobenzimidate ester is added to the reaction mixture as its hydrogen iodide salt, or if equivalent amounts of free ester and of potassium iodide are used (which amounts to the same thing since the free ester is effectively completely protonated at the acidities employed), then the observed kinetics of hydrolysis differ from those found when free ester is used alone. Four principal differences are found.

(i) Except at very low chloride concentrations, the rate of hydrolysis becomes independent of [AuCl$_4^-$]$_{\text{stoich}}$, provided this latter concentration is kept in excess of [I$^-$].

(ii) Except when [Cl$^-$] ⟶ 0, the disappearance of ester obeys second-order kinetics.

(iii) Except when [Cl$^-$] ⟶ 0, the velocity of hydrolysis under given conditions is appreciably faster than that in the absence of iodide ions, the latter rate being usually negligible by comparison.

(iv) An increase in chloride ion concentration over the range 0—2.0M, with the concentration of the other reagents fixed, leads to a maximum in the rate at [Cl$^-$] $\simeq$ 0.15M. This effect is found both at constant and at variable ionic strength. As in the absence of iodide ions, there occurs an eventual fall in the observed rate constant (here k_2) at higher chloride ion concentrations, but even so the disappearance of ester remains substantially faster than in the absence of iodide ions.

TABLE 2

Experiments with *N*-cyclohexylmethylthiobenzimidate hydrogen iodide (B)

[Ester]$_{\text{initial}}$ = [I$^-$]$_{\text{initial}}$ = 5.0 × 10^{-5}M except as stated; temperature 23°; solvent 2% v/v ethanol–water

Effect of [AuCl$_4^-$]
(i) [Cl$^-$] = 2.0M, 10^3[H$_3$O$^+$] = 1.82M

10^4[AuCl$_4^-$]/M	1.0	2.0	2.5	3.0	3.75
k_2/l mol^{-1} s^{-1}	3.9	3.8	4.2	3.9	3.7
				(3.8) *	

(ii) [Cl$^-$] = 0.10M, 10^3[H$_3$O$^+$] = 1.82M

10^4[AuCl$_4^-$]/M	1.0	3.0	
k_2/l mol^{-1} s^{-1}	42.0	40.5	(42.0) †

(iii) [Cl$^-$] = 0.0M, 10^3[H$_3$O$^+$] = 1.82M

10^4[AuCl$_4^-$]/M	2.5	3.0	3.5	4.0
10^4k_{obs}/s^{-1}	1.30	1.42	1.70	1.92

Effect of [H$_3$O$^+$]
(i) [Cl$^-$] = 2.0M, 10^4[AuCl$_4^-$] = 3.0M

10^2[H$_3$O$^+$]/M	0.10	0.18	0.27	0.91	1.82
k_2/l mol^{-1} s^{-1}	10.3	3.9	3.3	1.5	0.75
10^2[H$_3$O$^+$]/M	2.72	4.50	9.00	18.1	
k_2/l mol^{-1} s^{-1}	0.65	0.33	0.22	0.14	

(ii) [Cl$^-$] = 0.10M, 10^4[AuCl$_4^-$] = 3.0M

10^2[H$_3$O$^+$]/M	0.18	0.91	9.00	90.0
k_2/l mol^{-1} s^{-1}	50	29	4.3	1.0

(iii) [Cl$^-$] = 0.0M, 10^4[AuCl$_4^-$] = 3.0M

10^3[H$_3$O$^+$]/M	1.00	1.82	9.12	45.6
10^4k_{obs}/s^{-1}	1.92	2.11	2.03	1.84

Effect of [Cl$^-$]
(i) 10^3[H$_3$O$^+$] = 1.82M, 10^4[AuCl$_4^-$] = 3.0M, ionic strength = 2.5M (added NaClO$_4$)

10[Cl$^-$]/M	0.10	0.20	0.50	1.00	2.00
k_2/l mol^{-1} s^{-1}	5.0	8.1	21	26	20
10[Cl$^-$]/M	4.00	5.00	10.0	20.0	
k_2/l mol^{-1} s^{-1}	9.3	7.6	4.4	3.8	

(ii) 10^3[H$_3$O$^+$] = 1.82M, 10^4[AuCl$_4^-$] = 3.0M

10[Cl$^-$]/M	0.10	0.20	0.40	1.0	2.0	3.0
k_2/l mol^{-1} s^{-1}	8.0	12	17	44	69	63
10[Cl$^-$]/M	5.0	10.0	20.0			
k_2/l mol^{-1} s^{-1}	35	16	3.9			

* 10^5[Ester] = 2.5M.
† 10^5[I$^-$] = 10.0M.
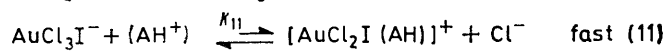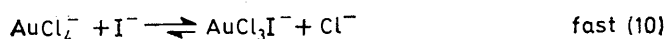
The effects of changes in [H$_3$O$^+$], at different chloride ion concentrations, follow the same pattern in the presence as in the absence of iodide ions. These various findings are illustrated by results in Table 2 and Figure 4. As [Cl$^-$] ⟶ 0 the effect of iodide ions is greatly reduced and at [Cl$^-$] = 0 the kinetic behaviour is similar

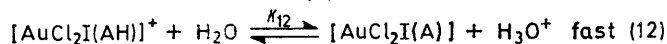to that found in the absence of iodide, including a return to first-order loss of ester (Table 2).

We find that iodide owes its catalytic effect to reaction with chlorogold(III) species. At moderate free chloride ion concentrations, and in the absence of the thio-benzimidate ester, iodide ions react rapidly with an excess of $AuCl_4^-$ according to $1:1$ stoicheiometry, probably as in the overall equation (8). (Reduction of Au^{III} might be expected to lead to a $1:2$ stoicheiometry.[3]) At high chloride ion concentrations the reaction is very rapid and may involve $AuCl_6^{3-}$ [equation (9)]. Chloride ions evidently catalyse the entry of

$$AuCl_4^- + I^- \longrightarrow AuCl_3I^- + Cl^- \qquad (8)$$

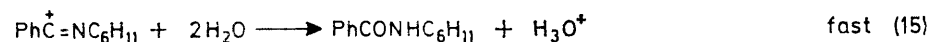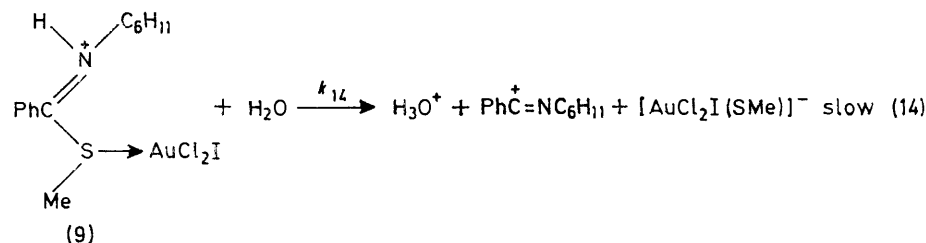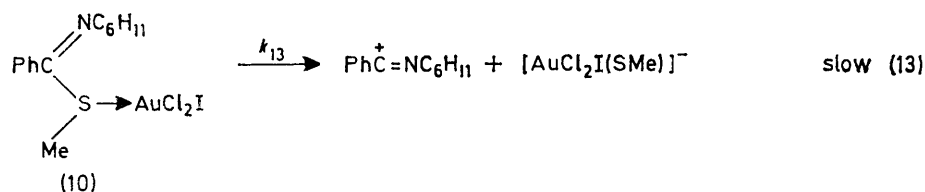$$AuCl_6^{3-} + I^- \longrightarrow AuCl_5I^{3-} + Cl^- \qquad (9)$$

iodide. These monoiodo-complexes do not absorb light significantly at 315 nm so that their formation from the chlorogold species can easily be followed. Indeed the changes in the u.v. spectra involved are very different from those found in the presence of an excess of iodide, when reduction of the gold(III) species is important.[3]

of the free ester (A). At the very low chloride ion concentrations where aquogold complexes exist,[4] ageing
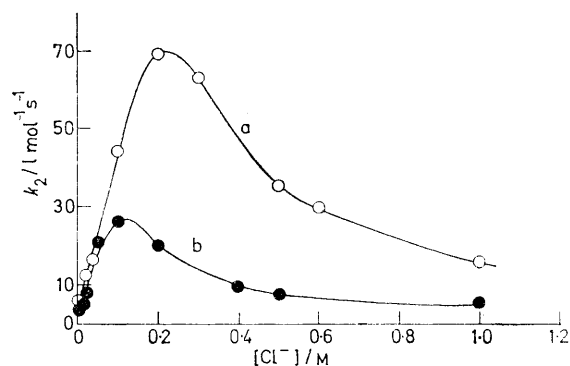

FIGURE 4 Effect of chloride ions in the presence of iodide ions: a, variable ionic strength; b, constant ionic strength (2.50M)

for 24 h is needed and the resulting iodogold complex (or a decomposition product) is at least partly precipitated in colloidal form. The fall in k_2 as $[Cl^-] \longrightarrow 0$

$$AuCl_4^- + I^- \rightleftharpoons AuCl_3I^- + Cl^- \qquad \text{fast (10)}$$

$$AuCl_3I^- + (AH^+) \xrightarrow{K_{11}} [AuCl_2I\,(AH)]^+ + Cl^- \qquad \text{fast (11)}$$

$$(9)$$

$$[AuCl_2I(AH)]^+ + H_2O \xrightarrow{K_{12}} [AuCl_2I(A)] + H_3O^+ \qquad \text{fast (12)}$$

$$(10)$$

$$\underset{\underset{\underset{Me}{|}}{\overset{S \rightarrow AuCl_2I}{\diagdown}}}{\underset{PhC}{\overset{\diagup NC_6H_{11}}{\diagdown}}} \xrightarrow{k_{13}} Ph\overset{+}{C}=NC_6H_{11} + [AuCl_2I(SMe)]^- \qquad \text{slow (13)}$$

$$(10)$$

$$\underset{\underset{\underset{Me}{|}}{\overset{S \rightarrow AuCl_2I}{\diagdown}}}{\underset{PhC}{\overset{\diagup}{\diagdown}}}\overset{H}{\underset{}{\diagdown}}\overset{+}{\underset{N}{\diagup}}\overset{C_6H_{11}}{} + H_2O \xrightarrow{k_{14}} H_3O^+ + Ph\overset{+}{C}=NC_6H_{11} + [AuCl_2I(SMe)]^- \quad \text{slow (14)}$$

$$(9)$$

$$Ph\overset{+}{C}=NC_6H_{11} + 2H_2O \longrightarrow PhCONHC_6H_{11} + H_3O^+ \qquad \text{fast (15)}$$

When $[Cl^-] \gtrsim 0.1M$ the rate of formation of the iodo-gold complexes is sufficient for this process to be essentially complete before a significant fraction of the ester is hydrolysed so that under these conditions it is possible to add the ester as its hydrogen iodide (B). At lower chloride concentrations it is necessary to make up reaction mixtures containing $AuCl_4^-$, potassium iodide, and all the other components except the ester, and allow these to age sufficiently for the iodogold complex to form before initiating the hydrolysis by the final addition

(Figure 4) arises partly therefore from the removal of gold and iodide by this precipitation; but the precipitation cannot account for the whole of the fall in k_2 for when $[Cl^-] \gtrsim 0.02M$ the mixtures remain homogeneous. We conclude therefore that the species $[AuCl_2I(H_2O)]$ {or $[AuCl_2I(OH)]^-$} is less effective in promoting ester hydrolysis than is $[AuCl_3I]^-$.

We suggest then that in the presence of iodide ions the tetrachlorogold(III)-promoted hydrolysis of thio-benzimidate esters proceeds via routes such as (10)—(15),

exactly analogous to those in processes (2)—(6) except that equilibrium (11) probably lies substantially further to the right than when I^- is absent, owing to the flocking effect[8] shown by the soft ligands I and S, *i.e.* the presence of I attached to the gold atom leads to the co-ordination of more of the S-ester than would otherwise occur. We assume that any change in the rate of the slow steps [*e.g.* (13) and (14)] arising from the presence of iodide is either also in a favourable direction, or small compared with the benefits arising from the shift in equilibrium positions.
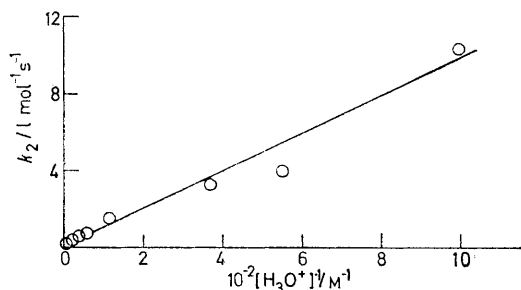

FIGURE 5   Plot of k_2 against $1/[H_3O^+]$

Route (10)—(15) which will probably be dominant (see p. 1281) when $[Cl^-] \gtrsim 0.04M$ leads to the rate equation (16) [analogous to equation (7)]. At fixed values of

$$-d[Ester]/dt = (k_{14}K_{11} +$$
$$k_{13}K_{11}K_{12}/[H_3O^+])[AuCl_3I^-][Ester]/[Cl^-]   (16)$$

$[H_3O^+]$ and $[Cl^-]$, and when $[I^-]_{init} = [Ester]_{init}$, equation (16) reduces to (17), in agreement with the form found experimentally. In equation (17) $k_2 = (k_{14}K_{11} +$

$$-d[Ester]/dt = k_2[Ester]^2   (17)$$

$k_{13}K_{11}K_{12}/[H_3O^+])/[Cl^-]$ or, at a constant value of $[Cl^-]$, $k_2 = k'_{14} + k'_{13}/[H_3O^+]$. Figure 5 shows a plot of k_2 against $1/[H_3O^+]$ under such conditions; a (reasonable) straight line is evident, as predicted. As in the absence of iodide ions, the effect of changes in $[H_3O^+]$ when $[Cl^-] = 0$ is much less marked than at high concentrations (Table 2). A similar explanation can be used

to account for this result (see p. 1282). Also the fall in velocity on moving from moderate to high chloride concentrations will be due, as before, to the displacement of ester from the gold atom by the large concentration of chloride ions. In the presence of co-ordinated iodide this displacement is less effective and the observed rates remain higher than in the absence of iodide even at high chloride ion concentrations.

The second-order behaviour found in the presence of iodide ions when equivalent amounts of ester and I^- are used, arises from the consumption of the iodogold complexes as the ester reacts. Actually, as noted in the Experimental section, approximately two molecules of gold complex are eventually consumed per molecule of ester, but in the presence of an excess of $AuCl_4^-$, as in our experiments, the second molecule of gold complex is doubtless taken from this excess. At low chloride ion concentrations, when the catalysis by iodide becomes inoperative or negligible, the residual rate will be due simply to the excess of gold species and the reaction order in ester will be expected to return to unity, as found.

Experiments with Other Soft Anions.—It is evident that the effect of iodide arises because, in the presence of sufficient chloride ions, a new gold complex is rapidly formed which promotes the hydrolysis of the thiobenzimidate ester more effectively. Other soft anions might be expected to behave similarly. We have tested bromide, cyanide, and thiocyanate ions. As anticipated[3,9] all these anions react with $AuCl_4^-$ in water but only bromide provides any enhancement of the ester hydrolysis, it being, however, less effective than iodide (Table 1). The reason for the complete inactivity of the cyanide and thiocyanate ions is not understood but the fact that bromide ions, which do not reduce $AuCl_4^-$, do provide significant catalysis of the ester hydrolysis, provides an additional ground for rejecting a reductive path for the iodide catalysis.

[8] R. G. Pearson, *Science,* 1966, **151**, 172.
[9] L. Cattalini, A. Orio, and M. L. Tobe, *J. Amer. Chem. Soc.,* 1967, **89**, 3130.