Reactions of Silver Ions with Thiobenzamides in Aqueous Solution

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In aqueous acid solution, in the presence of an excess of silver ions, thiobenzamides form 1 *S*-amide : 1 Ag^+ complexes stoicheiometrically. For thiobenzamide the decomposition of the 1 : 1 complex leads to silver sulphide and benzonitrile and for *N*-cyclohexylthiobenzamide to silver sulphide and the *O*-amide. For both thiobenzamide and *N*-cyclohexylthiobenzamide the kinetic forms suggest mechanisms of decomposition similar to those proposed for the corresponding decompositions of *S*-amide–Hg^{2+} complexes. These mechanisms involve the ionisation of the *S*-amides' *N*-hydrogen atoms.

THIS paper extends to silver ions our earlier work on the reactions between mercury(II) [1] and copper(II) [2] ions and thiobenzamides. Previous work shows (i) that thiobenzamide and similar thioamides when added to solutions of silver salts usually lead to isolable, solid 1 : 1-complexes [3,4] {*e.g.* $[PhC(NH_2)=S\rightarrow Ag]^+NO_3^-$} and (ii) that thioacetamide forms various *S*-amide–Ag^+ complexes which undergo subsequent decomposition to silver sulphide and an organic product.[5,6] This product has been variously suggested to be the *O*-amide, the carboxylic acid, or the nitrile. It has been shown [5] (qualitatively) that, at a fixed silver ion concentration, the rate of silver sulphide formation is retarded by an increase in $[H_3O^+]$, or by the presence of an excess of thioacetamide, the latter effect probably arising from the conversion of the 1 : 1-complex to complexes containing a higher *S*-amide : Ag^+ ratio, since it is believed that the 1 : 1-complex is the most reactive of the various possible complexes.[6] It has also been claimed that these direct reactions between thioacetamide and silver ions dominate at pH > 3, whilst at lower pH the formation of silver sulphide arises indirectly *via* the preliminary hydrogen ion-catalysed hydrolysis of the *S*-amide to hydrogen sulphide.[5]

EXPERIMENTAL

Materials.—Thiobenzamide, *N*-cyclohexylthiobenzamide, benzonitrile, *N*-cyclohexylbenzamide, perchloric acid, and ethanol were previous samples.[1,2] Silver perchlorate was from B.D.H. and aluminium nitrate was AnalaR grade. The amides are poorly soluble in water and were always used as stock solutions in pure ethanol to facilitate their dissolution in aqueous mixtures.

Complex Formation in Solution and Final Reaction Products.—In aqueous solution the free *S*-amides (10^{-4}M) absorb with moderate intensity [1] at *ca.* 250 and *ca.* 285 nm. The spectra are effectively unchanged by the presence of 0.2M-perchloric acid. The additional presence of silver perchlorate (10^{-5}—4×10^{-4}M) leads to an increase in absorption in the 270—290 nm region, arising from the formation of a complex between the silver ion and the *S*-amide. The optical density changes (Figure 1) indicate [7] that for thiobenzamide a 1 : 1-complex (ε 9 200 at 290 nm) is formed stoicheiometrically at all concentrations used (*i.e.* the formation constant is very large). With *N*-cyclohexylthiobenzamide the formation of both a 2 *S*-amide : 1 Ag^+ (ε 9 500 at 278 nm) and a 1 : 1-complex (ε 9 800 at 278 nm) is detected (Figure 2) Again both the formation constants are large. At higher acidities the observed extinction coefficients are larger, and at 1—2M-$HClO_4$ reach maximum values *ca.* 20% greater than those quoted for 0.2M-acid. The changes are compatible [1] with the complexes engaging in *N*-protonation equilibria [see equation (6)]. The thiobenzamide solutions were made up to contain 3% v/v of ethanol, but with the *N*-cyclohexyl derivative the complexes are much less soluble and a 30% v/v ethanol–water solvent was necessary to keep the mixtures homogeneous. A similar solvent was also used in the kinetic experiments with this compound.

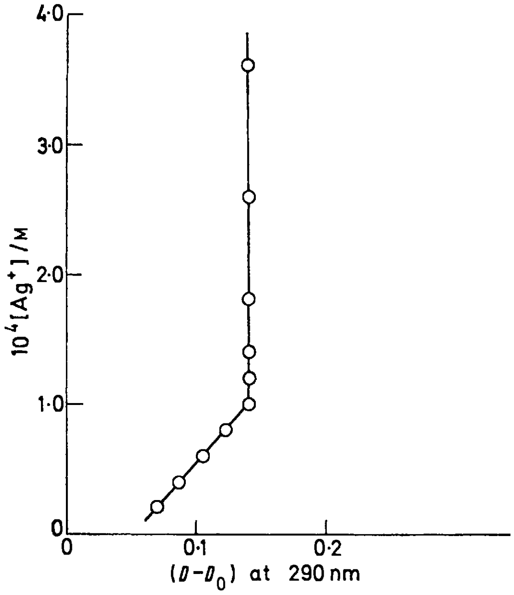

FIGURE 1 Complex formation between Ag^+ and $PhCSNH_2$ in 3% v/v EtOH–H_2O. $[PhCSNH_2]_0 = 10^{-4}$M

The *S*-amide–Ag^+ complexes detected spectroscopically are formed rapidly, but subsequently decompose to give silver sulphide and an organic product. The decomposition is faster the smaller the value of $[H_3O^+]$. At 0.2M-perchloric acid the decomposition is slow enough for accurate optical density measurements to be made of the initial complex formation without the need for extrapolation. Hence the inclusion of the acid. As the decomposition proceeds silver sulphide is formed and eventually coagulates. Thiobenzamide leads to benzonitrile in high yield as the organic product [reactions (1) and (2)] and *N*-cyclohexylthiobenzamide to the corresponding *O*-amide [reaction (3)].

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[2] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 953.

[3] F. Kasparek and J. Mollin, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2919.

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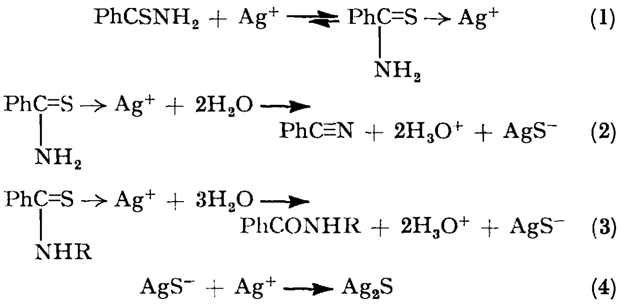
[7] A. E. Harvey and D. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

Kinetic Arrangements.—It is difficult to achieve satisfactory kinetic conditions for these reactions. Previous studies [5,6] have been very qualitative. With mercury [1] and copper [2] we worked with solutions which remained homogeneous throughout a run, but with the present system this proved impossible. The silver sulphide product is precipitated even when formed in relatively very low concentration, and appears initially in a colloidal form. This colloidal precipitate leads to powerful, heterogeneous autocatalysis, so that a simple kinetic form is unobtainable over any appreciable fraction of the reaction. By adding to the reaction mixtures a moderate concentration of aluminium ions, which help to coagulate the silver sulphide (but do not themselves catalyse the reaction) we have been able to reduce the auto-catalysis and to study kinetically the first 10% of each reaction without significant disturbance from it. We have partly off-set the inaccuracy introduced in only studying the initial phase of each run by conducting repeat experiments (usually three) for each set of conditions, and averaging the results. Apart from these special arrangements, our kinetic experiments were similar to those used for the corresponding reactions involving mercury(II) ions.[1] The silver ion concentration was kept in considerable excess over that of the *S*-amide. The first-order disappearance of the rapidly formed *S*-amide–Ag⁺ complex was followed spectroscopically. The concentration conditions were such that the *S*-amide was present exclusively as the 1 : 1-complex. That its disappearance is truly first-order is confirmed by the similarity of the rate constants observed at different initial *S*-amide (*i.e.* complex) concentrations. The quoted (average) first order-rate constants, k_{obs}, can be reproduced to within ±10%. Our results for thiobenzamide and *N*-cyclohexyl thiobenzamide are in Tables 1 and 2 respectively. Most experiments were made at 4.0°.



$$\mathrm{PhCSNH_2 + Ag^+ \rightleftharpoons \underset{\displaystyle NH_2}{PhC{=}S} \rightarrow Ag^+} \qquad (1)$$

$$\mathrm{\underset{\displaystyle NH_2}{PhC{=}S} \rightarrow Ag^+ + 2H_2O \longrightarrow PhC{\equiv}N + 2H_3O^+ + AgS^-} \qquad (2)$$

$$\mathrm{\underset{\displaystyle NHR}{PhC{=}S} \rightarrow Ag^+ + 3H_2O \longrightarrow PhCONHR + 2H_3O^+ + AgS^-} \qquad (3)$$

$$\mathrm{AgS^- + Ag^+ \longrightarrow Ag_2S} \qquad (4)$$

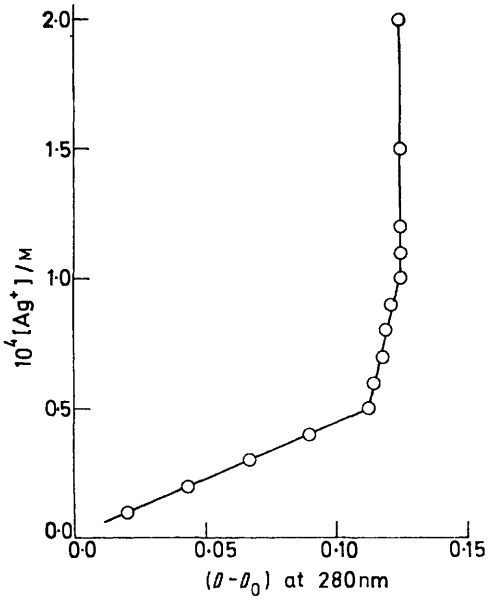


FIGURE 2 Complex formation between Ag^+ and $PhCSNHC_6H_{11}$ in 30% v/v EtOH–H_2O. $[PhCSNHC_6H_{11}]_0 = 10^{-4}M$

RESULTS AND DISCUSSION

Our results for thiobenzamide and *N*-cyclohexylthiobenzamide show that in the presence of an excess of silver ions these *S*-benzamides are stoicheiometrically converted into 1 *S*-amide : 1 Ag⁺ complexes whose first-order rate of decomposition to silver sulphide at a given temperature is (i) unaffected by changes in $[Ag^+]_{free}$, and (ii) progressively reduced by the addition of increasing amounts of hydrogen ion, until levelling out at

TABLE 1

Kinetic experiments with thiobenzamide

Solvent 3% v/v ethanol–water; $[S\text{-amide}]_{initial} = 10^{-4}M$, except where specified; $[Al^{3+}] = 0.02M$; k_{obs} = observed first-order rate constant for loss of $[1\ S\text{-amide}{:}1\ Ag^+\text{-complex}]_{total}$ (see text)

(i) Effect of initial thiobenzamide concentration at 4.0°

$10^3[Ag^+] = 2.0M$; $[H_3O^+] = 0.90M$

$10^4[S\text{-amide}]_{initial}/M$	0.50	1.0	1.5
k_{obs}/h^{-1}	0.010	0.012	0.012

(ii) Effect of free silver ion concentration at 4.0°

$[H_3O^+] = 0.90M$

$10^4[Ag^+]_{free}/M$	9.0	19	29	39	59
k_{obs}/h^{-1}	0.011	0.011	0.010	0.012	0.012

(iii) Effect of hydrogen ion concentration at 4.0°

$10^3[Ag^+] = 2.0M$

$[H_3O^+]/M$	0.05	0.17	0.36	0.54	0.72	1.08
k_{obs}/h^{-1}	0.11	0.046	0.023	0.017	0.012	0.0095
$[H_3O^+]/M$	1.44	1.80	2.16	3.24		
k_{obs}/h^{-1}	0.012	0.0081	0.0090	0.012		

(iv) Effect of temperature at various values of $[H_3O^+]$

$10^3[Ag^+] = 2.0M$

$[H_3O^+]/M$	0.54	0.81	0.90	1.08	1.80	2.70
k_{obs}/h^{-1} (at 11.0°)	0.027	0.021	0.020	0.016		0.016
k_{obs}/h^{-1} (at 18.0°)		0.030	0.025	0.025	0.024	0.021

TABLE 2

Kinetic experiments with *N*-cyclohexylthiobenzamide

$[S\text{-amide}]_{initial} = 10^{-4}M$; solvent 30% v/v ethanol–water; $[Al^{3+}] = 0.02M$

(i) Effect of $[H_3O^+]$

(a) At 4.0°

$[H_3O^+]/M$	0.05	0.10	0.15	0.20	0.25	0.30	0.50	0.60
$10^2k_{obs}/h^{-1}$	5.8	3.0	2.3	1.6	1.3	1.1	0.68	0.58
$[H_3O^+]/M$	0.70	0.90	1.00	1.35	1.80	2.30	2.70	
$10^2k_{obs}/h^{-1}$	0.57	0.52	0.50	0.42	0.35	0.30	0.25	

(b) At 17.0°

$[H_3O^+]/M$	0.45	0.90	1.35	1.80	2.30
$10^2k_{obs}/h^{-1}$	1.8	1.0	0.88	0.69	0.70

(ii) Effect of free silver ion concentration at 4.0°

$[H_3O^+] = 0.50M$

$10^4[Ag^+]_{free}/M$	24	39	49
$10^2k_{obs}/h^{-1}$	0.68	0.74	0.68

a minimum value. The effect on the rate of changes in $[H_3O^+]$ is similar to those observed with the mercury(II) [1] and copper(II) [2] ion systems, except that the minimum value is reached when $[H_3O^+] \simeq 1.0$M. For the mercury(II) ion reaction the corresponding concentration was *ca.* 2.0M, and for the copper(II) ion reaction *ca.* 0.015M. Our present results can all be explained by reactions (5)—(11). This scheme is similar to that suggested for the mercury(II) ion reaction [1] except that for the silver system only 1 : 1-complexes are involved. [Metal-bound water molecules have been omitted for simplicity. It is unlikely [1,2] that equilibria such as $Ag(H_2O)_n^+ + H_2O \rightleftharpoons Ag(H_2O)_{n-1}OH + H_3O^+$ will be involved at the acidities used.] When R = H

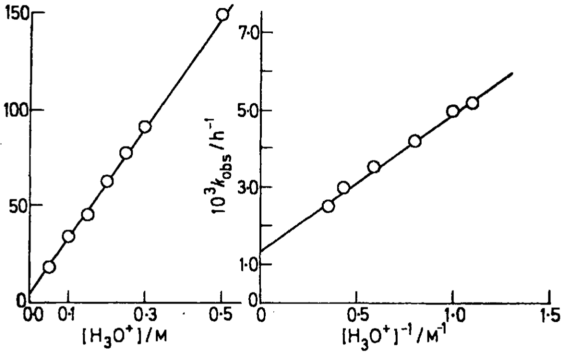


FIGURE 3 Plots of equations (14) and (15) for *N*-cyclohexylthiobenzamide at 4.0°

TABLE 3

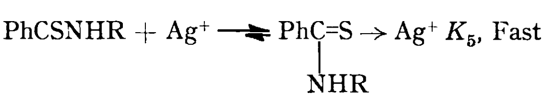
Derived kinetic parameters

(a) Thiobenzamide

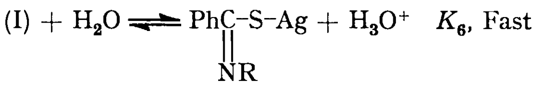
	4.0°	11.0°	18.0°	$\Delta S^‡$/cal K^{-1} mol^{-1}	E_a/kcal mol^{-1}
k_7'/h^{-1}	0.0054	0.0076	0.015	−56 (±5)	9.0 (±1)
k_8/h^{-1}	0.20				
K_6/mol l^{-1}	0.036				

(b) *N*-Cyclohexylthiobenzamide

	4.0°	17.0°	$\Delta S^‡$/cal K^{-1} mol^{-1}	E_a/kcal mol^{-1}
k_7'/h^{-1}	0.0012	0.0024	*ca.* −60	*ca.* 8.5
k_8/h^{-1}	0.30			
K_6/mol l^{-1}	0.0115			


$$PhCSNHR + Ag^+ \rightleftharpoons \underset{NHR}{PhC}{=}S \rightarrow Ag^+ \quad K_5,\ \text{Fast} \quad (5)$$

(I)


$$(I) + H_2O \rightleftharpoons \underset{NR}{\overset{}{PhC}}{-}S{-}Ag + H_3O^+ \quad K_6,\ \text{Fast} \quad (6)$$

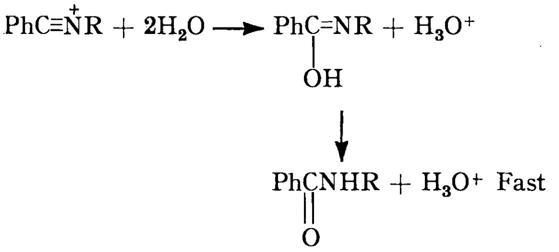
(II)

$$(I) + H_2O \longrightarrow PhC{\equiv}\overset{+}{N}R + H_3O^+ + AgS^- \quad k_7,\ \text{Slow} \quad (7)$$

$$(II) \longrightarrow PhC{\equiv}\overset{+}{N}R + AgS^- \quad k_8,\ \text{Slow} \quad (8)$$

reactions (7) and (8) will be followed by (9), but when R = cyclohexyl by (10). For the experimentally observed loss of the 1 : 1-complex (*i.e.* of $\{[(I)] + [(II)]\}$) the scheme predicts equation (13). Since it is probable that $k_8 > k_7'$, therefore when $[H_3O^+]$ is small equation (13) is likely to approximate to (14), and when $[H_3O^+]$ is large to (15).

$$PhC{\equiv}\overset{+}{N}H + H_2O \rightleftharpoons PhCN + H_3O^+ \quad \text{Fast} \quad (9)$$


$$PhC{\equiv}\overset{+}{N}R + 2H_2O \longrightarrow \underset{OH}{PhC}{=}NR + H_3O^+ \longrightarrow \underset{O}{\overset{}{PhC}}NHR + H_3O^+ \quad \text{Fast} \quad (10)$$

$$AgS^- + Ag^+ \longrightarrow Ag_2S \quad \text{Fast} \quad (11)$$

Hence the

$$-\{d[(I)]/dt + d[(II)]/dt\} = k_7[(I)][H_2O] + k_8[(II)]$$
$$= k_7'[(I)] + k_8[(II)] \quad (12)$$
$$= k_{obs}\{[(I)] + [(II)]\}$$

where $k_{obs} = (k_8K_6 + k_7'[H_3O^+])/(K_6 + [H_3O^+])$ (13)

$$\frac{1}{k_{obs}} = \frac{1}{k_8} + \frac{[H_3O^+]}{K_6k_8} \quad (14)$$

$$k_{obs} = k_7' + K_6k_8/[H_3O^+] \quad (15)$$

scheme predicts that plots of $1/k_{obs}$ against $[H_3O^+]$ and of k_{obs} against $1/[H_3O^+]$, at low and high acid concentrations respectively, will be rectilinear. Examples of such plots are in Figure 3. The derived parameters (k_7', k_8, and K_6) for thiobenzamide and for *N*-cyclohexylthiobenzamide at 4.0° are in Table 3. The results at higher temperatures are sufficient to permit partial analyses and lead to values of k_7' at these temperatures; these values are also in Table 3, together with the Arrhenius parameters for reaction (7).

The results for the two amides are not strictly comparable owing to the difference in solvent used. However, if we ignore this for the purposes of a qualitative comparison, then consideration of the values in Table 3 shows that they are at least chemically sensible. First, K_6, for *N*-cyclohexylthiobenzamide is smaller than for thiobenzamide as would be expected, the cyclohexyl group rendering the secondary amide the less acidic of the two. Secondly, as suggested above, for both compounds $k_8 > k_7'$. Thirdly, k_8 for the cyclohexyl derivative is greater than k_8 for the unsubstituted compound; this might be anticipated from the additional electron release available, which can facilitate the departure of AgS^-. Fourthly, k_7 for *N*-cyclohexylthiobenzamide is less than k_7 for thiobenzamide. The probable reason for this reversal of reactivity is that in reaction (7) not only is the departure of AgS^- involved but also the simultaneous approach of a water molecule and the loss of a proton; this latter event will be hindered electronically (and possibly sterically) by the cyclohexyl group. The large negative value found for $\Delta S^‡$ for reaction (7) is surprising and perhaps suggests that more than one water molecule is in fact involved. It is evident, however, that the proposed mechanism is, in general, compatible with the experimental results.

Our studies as a whole suggest that the ions Hg^{2+}, Cu^{2+}, and Ag^{+} all display mechanisms which are variations upon a common scheme, these variations being sensibly related to the chemistry of the individual ions. In behaviour and reactivity Ag^{+} lies between Hg^{2+} and Cu^{2+}; a precisely meaningful numerical comparison of their reactivities is, however, impracticable owing to the complexity of the mechanisms.

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