Kinetics and Mechanism of the Reaction between Copper(II) Ions and Thiobenzamide in Aqueous Solution

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The reaction between thiobenzamide and copper(II) ions in aqueous perchloric acid leads to benzonitrile and copper(II) sulphide. With N-substituted thiobenzamides the organic product is the corresponding O-amide. At 60° and with $[HClO_4] \gtrsim$ 0·5M, the thiobenzamide reaction obeys the rate equation $-d[S\text{-amide}]/dt = [S\text{-amide}] [Cu^{2+}]$ (8.2 + 0·063/$[H_3O^+]$) mol l^{-1} h^{-1}. A mechanism is suggested which involves the rate-determining decompositions of both a 1 S-amide: 1 Cu^{2+} complex and of its deprotonated form. This mechanism is similar in outline, but different in detail, from that probable for the corresponding reaction involving mercury(II) ions, which is ca. 2 × 10^5-fold faster under comparable conditions. N-Cyclohexyl thiobenzamide reacts faster than does thiobenzamide with Hg^{2+}, but slower with Cu^{2+}. The reasons for these differences are discussed. The copper(II) sulphide product can be precipitated in colloidal form and then leads to powerful heterogeneous autocatalysis. This effect is relatively unimportant at temperatures $\gtrsim$50°.

WE reported recently [1] on the mercury(II) ion promoted decomposition of thiobenzamides. We deal now with the corresponding reaction involving copper(II) ions. Little is known about this type of process. Three studies exist. Two [2] show that thioacetamide or thiobenzamide added to an aqueous Cu^{2+}–hydrogen halide mixture leads to the precipitation of an S-amide–$[Cu(halide)]^0$ complex, although with nitric or sulphuric acid in place of the hydrogen halide what is probably copper(II) sulphide is precipitated without evidence of intermediate complex formation. The third,[3] preliminary report concerns the kinetics of such precipitations under various conditions of pH. The organic product was not identified in any of these studies and there has been no discussion of the reaction mechanism.

EXPERIMENTAL

Materials.—Pure samples of thiobenzamide, N-cyclohexylthiobenzamide, N-thiobenzoylpiperidine, benzonitrile, N-cyclohexylbenzamide, and aqueous perchloric acid were obtained as previously described.[1] Copper(II) perchlorate hexahydrate was B.D.H. reagent grade material; carbon tetrachloride and ethanol were of AnalaR grade.

Products.—Preparative scale experiments, which simulated as far as possible the temperature and concentration conditions of the kinetic runs, showed that thiobenzamide and an aqueous Cu^{2+}–$HClO_4$ mixture leads to benzonitrile and copper(II) sulphide. The overall reaction is (1).

$$PhCSNH_2 + Cu^{2+} + 2H_2O \longrightarrow PhCN + CuS + 2H_3O^+ \quad (1)$$
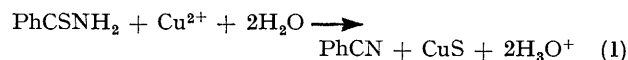
With N-cyclohexylthiobenzamide the product is the O-amide (2). Both reactions proceed in high (>90%) yield.

$$PhCSNHR + Cu^{2+} + 3H_2O \longrightarrow PhCONHR + CuS + 2H_3O^+ \quad (2)$$
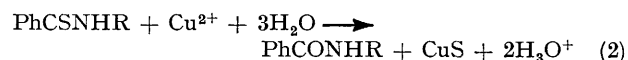
Kinetic Arrangements.—These were similar to those used for the mercury promoted reactions.[1] In all runs a small concentration of S-amide was added (as a stock solution in ethanol) to an excess of an aqueous $Cu(ClO_4)_2$–$HClO_4$ mixture. The resulting reaction mixture contained ca. 3% (v/v) of ethanol. The S-amides absorb [1] u.v. light strongly at 285 nm, where the products, and other reagents, absorb relatively feebly. In contrast to the mercury(II)

[1] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778.
[2] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1960, 82, 4169; F. Kasparek and J. Mollin, *Coll. Czech. Chem. Comm.*, 1960, 25, 2919.
[3] E. H. Swift and F. C. Anson, *Talanta*, 1960, 3, 296.

ion promoted reactions, with copper(II) ions there is no spectroscopic evidence for the rapid formation of a detectable quantity of an S-amide–Cu^{2+} complex; the disappearance of the S-amide with time can therefore be directly observed in the 285 nm region. The disappearance is very slow at room temperature and reactions were therefore conducted at ca. 60°. The thermostat was controlled to within $\pm 0.1°$. Another reason for conducting these reactions at temperatures $> 50°$ was that, as reaction proceeds, some copper(II) sulphide is precipitated. At lower temperatures this precipitate appears in a colloidal form and produces powerful, heterogeneous autocatalysis.[4] At temperatures $\gtrsim 50°$ this effect is much reduced and a clean first-order loss of S-amide can be observed over more than one half-life. The observed first-order rate constants, k_{obs}, were calculated from plots of $\log(D - D_\infty)$ against time, where D is the optical density at some chosen wavelength. Values of k_{obs} for thiobenzamide were reproducible to within $\pm 10\%$. Our results for various Cu^{2+} and perchloric acid concentrations are in the Table. The reactions with the N-substituted derivatives proved to be very slow even at 60°. Our results for these compounds are more qualitative $(\pm 15\%)$ and cover a smaller range of concentration conditions (Table).

RESULTS AND DISCUSSION

The Experimental section, and the results in the Table and Figure 1, show that for thiobenzamide the loss of S-amide is kinetically first order in S-amide and in copper-(II) ions, while the reaction order in the hydrogen ion is

to the hydrogen ion catalysed hydrolysis of thiobenzamide [5] whose rate is known to become significant at 60°

Reaction between copper (II) ions and thiobenzamides in aqueous perchloric acid at 59.5°

$[S\text{-amide}]_{initial}$ ca. 10^{-4}M; for k_{obs} see text; solvent, 3% (v/v) ethanol–water

(1) Thiobenzamide

(a) Effect of $[Cu^{2+}]$ with $[HClO_4]$ 0.0036M

$10^3[Cu^{2+}]$/M	0.50	1.0	1.5	2.0	3.0	5.0
$10k_{obs}$/h^{-1}	0.12	0.24	0.38	0.50	0.69	1.15

(b) Effect of $[HClO_4]$ with $[Cu^{2+}]$ 1×10^{-3}M

$10^2[HClO_4]$/M	0.05	0.10	0.15	0.20	0.25	0.30	0.40	0.50
10^2k_{obs}/h^{-1}	14	6.8	4.8	3.75	3.3	2.9	2.45	2.0
$10^2[HClO_4]$/M	0.60	0.70	0.80	0.95	1.2	1.4	1.5	2.0
10^2k_{obs}/h^{-1}	1.75	1.6	1.45	1.4	1.35	1.3	1.3	1.2
$10^2[HClO_4]$/M	2.5	4.5						
10^2k_{obs}/h^{-1}	1.1	0.85						

(2) N-Cyclohexylthiobenzamide ($[Cu^{2+}] = 1 \times 10^{-3}$M)

$10^2[HClO_4]$/M	0.00	0.05	0.18
10^2k_{obs}/h^{-1}	0.21	0.13	0.12

(3) N-Thiobenzoylpiperidine ($[Cu^{2+}] = 1 \times 10^{-3}$M)

$10^2[HClO_4]$/M	0.00	0.05	0.18
10^2k_{obs}/h^{-1}	0.05	0.035	0.030

when $[H_3O^+] \gtrsim 1$M. This hydrogen ion catalysed hydrolysis contributes negligibly to k_{obs} at lower concentration,[5] where the copper(II) ion promoted decomposition is dominant.

The variation of k_{obs} with $[H_3O^+]$ for the copper(II)

$$PhCSNH_2 + Cu^{2+} \rightleftharpoons \underset{\underset{(I)}{NH_2}}{PhC = S \rightarrow Cu^{2+}} \qquad \text{Fast, } K_3 \quad (3)$$

$$(I) + H_2O \rightleftharpoons \underset{\underset{(II)}{NH}}{PhC - S - Cu^+} + H_3O^+ \qquad \text{Fast, } K_4 \quad (4)$$

$$(I) + H_2O \rightleftharpoons \left[\text{Transition state} \right] \longrightarrow PhC \equiv N^+H + H_3O^+ + CuS \qquad \text{Slow, } k_5 \quad (5)$$

$$(II) \longrightarrow PhC \equiv N^+H + CuS \qquad \text{Slow, } k_6 \quad (6)$$

$$PhC \equiv N^+H + H_2O \rightleftharpoons PhCN + H_3O^+ \qquad \text{Fast} \quad (7)$$

$$\left[\text{or } PhC \equiv N^+R + 2H_2O \longrightarrow \underset{\underset{H}{|}}{PhCONR} + H_3O^+ \qquad \text{Fast} \right]$$
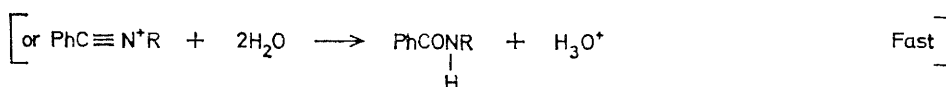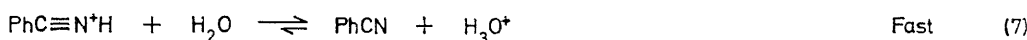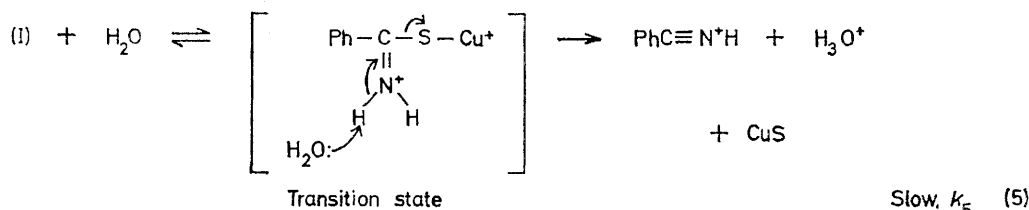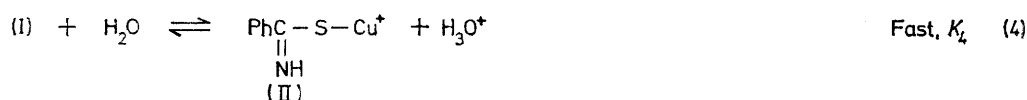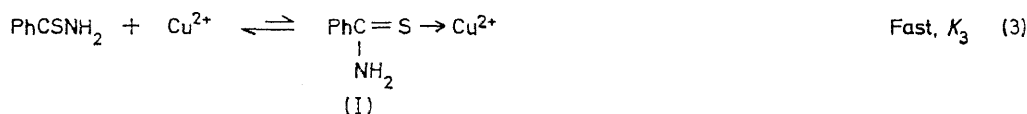
variable. At very low values of $[H_3O^+]$, k_{obs} is approximately inversely proportional to this concentration, but when $[H_3O^+]$ has risen to 0.1M, k_{obs} has become largely independent of $[H_3O^+]$. At relatively high values of $[H_3O^+]$, k_{obs} begins to rise again. This latter effect is due

ion reaction is similar to that found for the analogous mercury(II) ion process and probably arises from the same type of effect.[1] Reactions (3)—(7), from which

[4] H. Flaska, Chem. Analyst, 1955, 44, 2.
[5] A. J. Hall and D. P. N. Satchell, J.C.S. Perkin II, 1974, 1077.

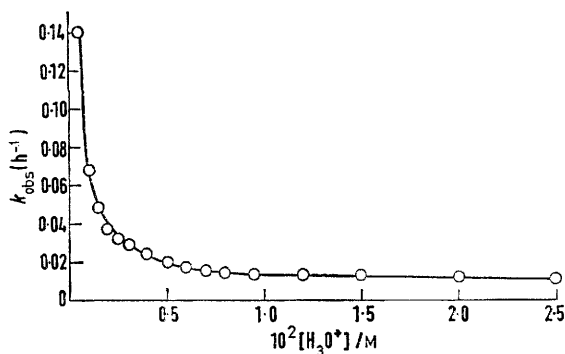solvating water molecules have been omitted for simplicity, can account for the present results.* This

FIGURE 1   Variation of k_{obs} with $[H_3O^+]$ at 59.5°

mechanism is a simplified version of that proposed for the mercury(II) ion reaction; it is simpler mainly because the rapid and stoicheiometric formation of $2S$-amide–M^{n+} complexes is not detected for Cu^{2+} under our conditions. Since only very small concentrations of 1 S-amide : 1 Cu^{2+} complexes can be formed here, the suggested slow steps differ from those probable for the mercury(II) ion reaction, where the rate-determining processes appear to involve the formation of similar 1 : 1 complexes from stoicheiometrically formed 2 S-amide : 1 Hg^{2+} complexes and free Hg^{2+} ions. Apart from this difference the proposed mechanisms are similar. The present scheme would not be expected to be very susceptible to changes in ionic strength.

Reactions (3)—(7) lead to the rate equation (8). A plot of equation (9) leads to a good straight line over the whole acidity range (Figure 2). The proposed mechanism is therefore compatible with the observed kinetic behaviour. Our values for the composite constants k'_5 and k'_6 are $8.2 \times 10^{-3}\,h^{-1}$ and $0.063 \times 10^{-3}\,mol\,l^{-1}\,h^{-1}$, respectively. Since k_6 would be expected to be com-

$$- d\,[S\text{-amide}]/dt = k_5[(I)] + k_6[(II)]$$

$$= (k_5K_3 + k_6K_3K_4/[H_3O^+])[Cu^{2+}]\text{-} \\ [S\text{-amide}] \quad (8)$$

$$k_{obs} = (k_5K_3 + k_6K_3K_4/[H_3O^+])[Cu^{2+}] \\ = k'_5 + k'_6/[H_3O^+] \quad (9)$$

* Equilibria like $[Cu(H_2O)_n]^{2+} + H_2O \rightleftharpoons [Cu(H_2O)_{n-1}OH]^+ + H_3O^+$ will only be expected to intrude at pH > 6.

parable or greater than k_5, it seems that $K_4 \gtrsim 10^{-2}$. This is reasonable in the light of the value of 0.7 obtained for the corresponding constant in the Hg^{2+} system [1]; Cu^{2+} probably engages the S-amide in a much weaker bond than does Hg^{2+} for a negligible concentration of complex appears to form in equilibrium (3). It can be calculated that the relative rates of the Hg^{2+} and Cu^{2+} reactions under similar conditions would be $ca.\ 2 \times 10^5 : 1$.

Some authors [2,6] believe that, in contrast to mercury(II), the copper(II) ion engages the S-amide's nitrogen atom as well as, or instead of, its sulphur atom. Our results with the N-cyclohexyl derivative suggest that this could be the case. The fact that this compound reacts $ca.$ 30-fold slower than does thiobenzamide itself in the present system, whereas with Hg^{2+} it reacts $ca.$ 12-fold faster than the unsubstituted compound, suggests that for the Cu^{2+} reaction an important steric effect opposes the polar effect of the cyclohexyl group, for the polar effect alone would be expected to lead to an increase in rate, as found in the mercury(II) ion reaction.
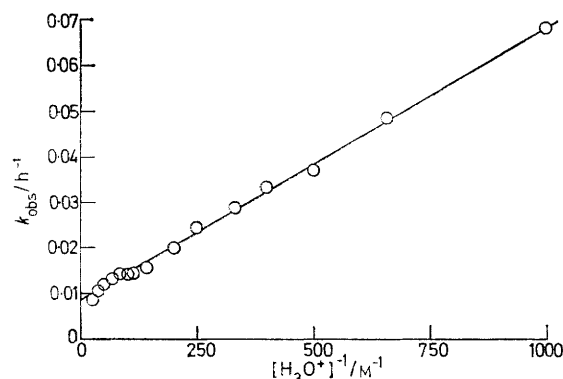

FIGURE 2   Plot of k_{obs} against $[H_3O^+]^{-1}$

If the copper ion must co-ordinate to nitrogen, as well as to sulphur, the N-cyclohexyl group could well lead to steric interference. Similar considerations could explain the even smaller rate found for N-thiobenzoylpiperidine, although the modification of the mechanism necessary for S-amides which cannot lose protons from nitrogen can also account for the lack of reactivity of this compound.[1]

[6] N. N. Greenwood and B. H. Robinson, J. Chem. Soc. (A), 1967, 511.