The Kinetics and Mechanism of the Reaction between Mercury(II) Ions and Thiobenzamides in Aqueous Solution

By **Alan J. Hall** and **Derek P. N. Satchell**, *Department of Chemistry, King's College, Strand, London WC2R 2LS

Thiobenzamide, *N*-cyclohexylthiobenzamide, and *N*-thiobenzoylpiperidine form complexes with the mercury(II) ion in dilute aqueous perchloric acid. The predominant complex in each case has a 2 *S*-amide : 1 Hg^{2+} stoicheiometry, but in the presence of a large excess of *S*-amide there is some evidence for the existence of a highly insoluble 4 : 1 complex. With an excess of mercuric ions, the 2 : 1 complexes are formed effectively quantitatively and any small amounts of 1 : 1 complex are not detectable. At 25°, the dissolved 2 : 1 complexes are relatively stable when $[H_3O^+] \gtrsim 0{\cdot}1$M and in the absence of added mercury(II) ions. In the presence of free mercury(II) ions, the complexes decompose to mercury(II) sulphide and an organic product in a process which, for thiobenzamide and *N*-cyclohexylthiobenzamide, is kinetically first order in the 2 : 1 complex and in mercury(II) ions. Increases in $[H_3O^+]$, at a fixed value of $[Hg^{2+}]$, retard the reaction, the rate falling eventually to a constant value. For thiobenzamide, the organic product is benzonitrile; for the *N*-substituted thiobenzamides, it is the corresponding *O*-amide. Mechanisms are suggested in which, for thiobenzamide and *N*-cyclohexylthiobenzamide, the slow steps are bimolecular reactions between free mercury(II) ions and the 2 : 1 complex or one of its deprotonated forms. The transiently formed 1 : 1 complexes decompose rapidly to the products in the absence of free *S*-amide. The mechanisms give a good account of the detailed dependence of the rate on $[H_3O^+]$. For thiobenzamide, the neutral species $[PhC(:NH)S]_2Hg$ is found to react *ca.* 600-fold faster with Hg^{2+} than does $\{[PhC(:S)NH_2]_2Hg\}^{2+}$. The overall sequence of reactivity at fixed $[Hg^{2+}]$, and at any value of $[H_3O^+]$, is *N*-cyclohexylthiobenzamide > thiobenzamide $\gg$ *N*-thiobenzoylpiperidine. This finding is also rationalised.

THIOAMIDES, especially thioacetamide, have been used [1] as alternatives to hydrogen sulphide for the precipitation of certain metals, notably Pb^{2+}, Hg^{2+}, Ag^+, Cu^{2+}, As^{3+}, and Cd^{2+}. Depending upon the circumstances, either a metal–*S*-amide complex is precipitated or the metal sulphide. In metal sulphide formation from aqueous solutions, two effects have been distinguished.[2,3] At pH $\lesssim$3 it is usually found that the *S*-amide is first hydrolysed to hydrogen sulphide whereupon metal sulphide precipitation follows rapidly, while at pH >3 there occurs a direct reaction between metal ion and *S*-amide which leads to the metal sulphide. This direct reaction is not observed for all the metals but for mercury(II) ions it is the dominant process even in quite highly acidic solutions. Complexes between certain mercury(II) salts, especially the chloride, and *S*-amides have been isolated.[4,5] These are considered to be stable in hydrochloric acid solutions, but to decompose to mercury(II) sulphide and an organic product when added to water. They have been taken to be either intermediates [4] in the direct formation of mercury(II) sulphide from mercury(II) ions and *S*-amides, or the reason that this latter reaction slows down in the presence of an excess of *S*-amide.[3] The organic product has been variously assumed to be the *O*-amide, the carboxylic acid, or the nitrile. Most previous work has used thioacetamide and has involved heterogeneous conditions. By employing thiobenzamides in low concentration in aqueous mercury(II) perchlorate–perchloric acid we have been able to examine the kinetic and other features of this general type of reaction under homogeneous conditions.

EXPERIMENTAL

Materials.—Thiobenzamide was a previous sample.[6] *N*-Cyclohexylthiobenzamide and *N*-thiobenzoylpiperidine

[1] R. N. Hurd and G. De La Mater, *Chem. Rev.*, 1961, **61**, 45.
[2] *E.g.*, D. V. Owens and E. H. Swift, *Talanta*, 1964, **11**, 1521.
[3] D. C. Taylor, D. M. Smith, and E. H. Swift, *Analyt. Chem.*, 1964, **36**, 1924.
[4] S. Petri and T. Lipiec, *Roczniki Chem.*, 1965, **39**, 1725.
[5] S. Ishikawa, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1928, **1**, 301; F. Kasparek and J. Mallin, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2919.
[6] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1974, 1077.

were prepared by Milligan and Swan's method.[7] They had m.p. 90 and 65·5° respectively and gave excellent microanalyses. Benzonitrile was the redistilled Fisons reagent. *N*-Cyclohexylbenzamide was prepared by the careful addition of an ethereal solution of cyclohexylamine to a two-fold excess of benzoyl chloride in the same solvent. The precipitated product was washed with dilute acid and with water, and recrystallised from a benzene–petroleum mixture, m.p. 147°. *N*-Benzoylpiperidine was prepared by Marvels and Laziers' method.[8] The product was a straw-coloured oil, b.p. 165—170° at 20 mmHg. Its i.r. and n.m.r. spectra were compatible with the structure of *N*-benzoylpiperidine. Carbon tetrachloride, anhydrous sodium carbonate, and perchloric acid were AnalaR reagents. Mercury(II) perchlorate was prepared as a stock solution (10^{-2}M) from the calculated quantities of mercury(II) oxide and aqueous perchloric acid.

U.v. Spectra.—In aqueous solution at 20°, thiobenzamide has absorption maxima at 290 (ε 8200) and 250 nm (8000). On addition of concentrated perchloric acid these are replaced by a single maximum at 275 nm (ε 15,100) due to *S*-protonated thiobenzamide.[6] In a solution of perchloric acid sufficiently dilute not to protonate the *S*-amide detectably,[6] the addition of mercury(II) ions leads to spectral changes similar to those brought about by concentrated perchloric acid. The new maximum occurs at 275 nm (ε 13,700 at 1·0M-$HClO_4$). Experiments modelled on those of Harvey and Manning,[9] using constant concentrations of *S*-amide (10^{-4}M) and perchloric acid (0·1M) and mercury(II) perchlorate concentrations ranging from 2×10^{-6} to 2×10^{-4}M, indicate that the absorption at 275 nm arises from the virtually stoicheiometric formation of a 2 *S*-amide : 1 Hg^{2+} complex. There is no spectroscopic evidence for a 1 : 1 complex, even in the presence of a considerable excess of mercury(II) ions. Tests showed that the formation of the 2 : 1 complex was not dependent on the presence of the perchloric acid. A moderate hydrogen ion concentration is desirable, however, to prevent the complex from decomposing too rapidly in those solutions containing an excess of mercury(II) ions (see below). Very similar results are obtained with the *N*-substituted thiobenzamides. *N*-Cyclohexylthiobenzamide has absorption maxima at 278 (ε 8300) and 245 nm (10,700) for the free amide, at 265 nm (ε 14,600) for the *S*-protonated species, and at 265 nm (ε 12,600 at 1·0M-$HClO_4$) for the 2 *S*-amide : 1 Hg^{2+} complex. For *N*-thiobenzoylpiperidine the values are 278 (ε 12,600) and 235 (10,000), 255 (ε 11,600), and 263 nm (ε 13,700 at 0·1M-$HClO_4$), respectively. With the *N*-substituted derivatives some evidence was found for the existence of a very insoluble 4 *S*-amide : 1 Hg^{2+} complex at low mercury(II) ion concentrations. This complex redissolves as the mercury(II) ion concentration is raised, being converted into the 2 : 1 complex. In those mixtures containing an effective (*i.e.* >[*S*-amide]/2) excess of mercury(II) ions, the complexes undergo relatively rapid further reaction to mercury(II) sulphide. This process is retarded by the presence of hydrogen ions. Hence the addition of perchloric acid (see above). In these mixtures reliable optical densities for the complex formation could be obtained by a short extrapolation to the time of mixing. Since *S*-amides are poorly soluble in water they were handled as stock solutions in ethanol. All the reaction mixtures used in these spectroscopic (and other) experiments contained *ca.* 3% (v/v) of ethanol. All u.v. spectra were measured with a Unicam SP 800 instrument.

Kinetic Arrangements.—(i) *Mercury promoted decomposition of thioamides.* An aqueous solution (2·5 ml) containing known concentrations of perchloric acid and of mercury(II) perchlorate was placed in a quartz cell (capacity 3 ml, path length 1 cm) in a thermostatted housing in the spectrophotometer. After thermal equilibrium was attained a small (*ca.* 0·1 ml) volume of a stock *S*-amide solution was injected into the cell, the contents rapidly shaken, and optical measurements begun. A blank cell contained all the reagents save the *S*-amide. Reaction mixtures normally contained a ten, or more, fold excess of mercury(II) ions over the *S*-amide (*ca.* 10^{-4}M) which, as noted above, is first rapidly and stoicheiometrically converted into the 2 *S*-amide : 1 Hg^{2+} complex. For thiobenzamide and *N*-cyclohexylthiobenzamide, as reaction proceeds the absorption due to the 2 : 1 complex falls, the products [mercury(II) sulphide and the nitrile or *O*-amide (see below)] absorbing only very slightly in this region. Provided that the mercury(II) ion is present initially in a ten, or more, fold excess, the loss of the 2 : 1 complex is an accurately first-order process over more than two half-lives. The reaction mixtures always remained homogeneous throughout the course of a run. For some of the mixtures mercury(II) sulphide precipitated eventually on standing. The observed first order rate constant, k_{obs}, was obtained from plots of log $(D_t - D_\infty)$ against time, where D represents optical density at some suitable wavelength. Values of k_{obs} were reproducible to within ±5%. Typical results for various perchloric acid and mercury(II) ion concentrations, and for different temperatures, are in Tables 1 and 2. Most experiments were at 6·0 ± 0·1°.

It proved impossible to obtain accurate rate measurements with *N*-thiobenzoylpiperidine since in this case mercury(II) ions also form a complex with the *O*-amide product and this complex absorbs very strongly in the same region as does the *S*-amide–mercury(II) ion complex. This fact, coupled with the slowness of the reaction for *N*-thiobenzoylpiperidine, made it difficult to obtain a reliable value for D_∞. We therefore have only qualitative results for *N*-thiobenzoylpiperidine (Table 2).

(ii) *Perchloric acid catalysed hydrolysis of* S-*amides.* Details of the rate of the hydrogen ion catalysed hydrolysis of thiobenzamide are known.[6] A few measurements along the same lines were made for the *N*-substituted derivatives. The reactions are very slow even at 60°: at 3·0M-perchloric acid $k_{obs} \simeq 0{\cdot}01$ h^{-1} for both compounds. We conclude that, under the conditions of concentration and temperature used in the mercury promoted decomposition, any concomitant hydrogen ion catalysed hydrolysis will be negligible.

Products.—(i) *Thiobenzamide and mercury*(II) *perchlorate.* Preparative scale experiments, at room temperature, using as far as possible concentration conditions similar to those of the kinetic runs, showed that the organic product was benzonitrile. The yield was 80—90%. No benzoic acid or *O*-amide was detected. The u.v. spectra taken at the completion of the kinetic runs always agreed within ±3% with those expected for complete conversion to benzonitrile which absorbs with low intensity at 277 (ε 850) and 271 nm (890). The inorganic product depends upon the perchloric acid concentration used. At concentrations below *ca.* 1·0M

[7] B. Milligan and J. M. Swan, *J. Chem. Soc.*, 1961, 1194.
[8] C. S. Marvels and A. Laziers, *Org. Synth.*, 1929, **9**, 16.
[9] A. E. Harvey and D. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

TABLE 1

Mercury(II) ion promoted decomposition of thiobenzamide in aqueous solutions

[Thiobenzamide]$_{initial} \simeq 10^{-4}$M; for k_{obs} see text; solvent = 3% v/v EtOH–H_2O

(a) Effect of $[Hg^{2+}]$ at 26·5°

(i) $[H_3O^+] = 0{\cdot}58$M

$10^3[Hg^{2+}]$/M	0·5	1·0	1·5	2·0	5·0
k_{obs}/min^{-1}	0·31	0·70	1·0	1·4	3·7

(ii) $[H_3O^+] = 3{\cdot}54$M

$10^3[Hg^{2+}]$/M	0·5	1·0	2·0	4·0
k_{obs}/min^{-1}	0·14	0·28	0·57	1·15

(b) Effect of $[H_3O^+]$ at $[Hg^{2+}] = 10^{-3}$M

(i) At 6·2°

$[H_3O^+]$/M	0·0018	0·0036	0·0054	0·0090	0·018
k_{obs}/min^{-1}	16·8	17·5	13·5	8·7	7·5
$[H_3O^+]$/M	0·038	0·054	0·090	0·18	0·36
k_{obs}/min^{-1}	6·0	3·8	2·5	1·15	0·45
$[H_3O^+]$/M	0·72	1·26	1·80	2·35	2·89
k_{obs}/min^{-1}	0·17	0·095	0·068	0·060	0·055

(ii) At 25·6°

$[H_3O^+]$/M	0·20	0·60	1·20	1·80	2·40
k_{obs}/min^{-1}	2·0	0·66	0·41	0·36	0·32
$[H_3O^+]$/M	3·00	3·60			
k_{obs}/min^{-1}	0·31	0·29			

(c) Effect of temperature at high acid concentrations ($[H_3O^+] = 3{\cdot}54$M; $[Hg^{2+}] = 0{\cdot}5 \times 10^{-3}$M)

T/°C	26·5	36·1	44·5
k_{obs}/min^{-1}	0·14	0·30	0·53

TABLE 2

Mercury(II) ion promoted decomposition of *N*-cyclohexylthiobenzamide and *N*-thiobenzoylpiperidine in aqueous solutions

(1) *N*-Cyclohexylthiobenzamide

[Thioamide]$_{initial} \simeq 10^{-4}$M; for k_{obs} see text; solvent = 3% v/v EtOH–H_2O

(a) Effect of $[Hg^{2+}]$ at $[H_3O^+] = 1{\cdot}12$M and 6·2°

$10^3[Hg^{2+}]$/M	0·5	1·0	1·5	2·0	2·5
k_{obs}/min^{-1}	0·55	1·1	1·7	2·2	2·6
$10^3[Hg^{2+}]$/M	3·0	4·0			
k_{obs}/min^{-1}	3·1	4·1			

(b) Effect of $[H_3O^+]$ at $[Hg^{2+}] = 10^{-3}$M and 6·2°

$[H_3O^+]$/M	0·075	0·15	0·23	0·30	0·45
k_{obs}/min^{-1}	4·2	3·1	2·7	2·1	1·4
$[H_3O^+]$/M	0·90	1·12	1·69	2·25	3·37
k_{obs}/min^{-1}	1·2	1·1	0·83	0·75	0·75
$[H_3O^+]$/M	3·92				
k_{obs}/min^{-1}	0·80				

(c) Effect of temperature

(i) $[H_3O^+] = 1{\cdot}12$M

T/°C	$[Hg^{2+}] = 0{\cdot}5 \times 10^{-3}$M ($k_{obs}$/min^{-1})	$[Hg^{2+}] = 10^{-3}$M (k_{obs}/min^{-1})
6·2	0·55	1·1
14·3	1·0	2·1
27·5	2·7	4·8

(ii) $[H_3O^+] = 3{\cdot}92$M and $[Hg^{2+}] = 10^{-3}$M

T/°C	6·2	14·3	27·5
k_{obs}/min^{-1}	0·80	1·5	4·2

(2) *N*-Thiobenzoylpiperidine

[Thioamide]$_{initial} \simeq 10^{-5}$M; tp 60°, for k_{obs} see text

With $[Hg^{2+}] = 10^{-3}$M and $[H_3O^+] = 1{\cdot}12$M then $k_{obs} \simeq 0{\cdot}2$ h^{-1}

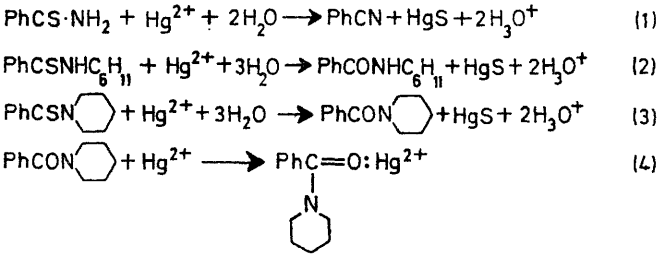
the principal product is mercury(II) sulphide, but at higher acid concentrations a mixed mercury sulphide perchlorate is precipitated on standing.

(ii) *N-Cyclohexylthiobenzamide and mercury(II) perchlorate.* Similar preparative experiments at room temperature led here to the isolation of the *O*-amide (yield *ca.* 90%) as the only detectable organic product. The inorganic product was essentially pure mercury(II) sulphide.

(iii) *N-Thiobenzoylpiperidine and mercury(II) perchlorate.* Owing to the slowness of the reaction, the preparative experiments were conducted at 60°. After 18 h a mixture containing initially a 10 : 1 mole ratio of mercury(II) perchlorate to the *S*-amide in 3M-perchloric acid was found to contain principally a material whose elemental analysis corresponded to Hg(*N*-benzoylpiperidine)$(ClO_4)_2$. This compound is a white solid, m.p. 190—193° (decomp.), whose i.r. and n.m.r. spectra are compatible [10] with its containing a tertiary *O*-amide co-ordinated to Hg^{2+}. A quantity of what was probably a complex mercury sulphide perchlorate was also isolated.

RESULTS AND DISCUSSION

The Overall Reaction.—The isolated products show that for thiobenzamide the overall reaction is (1), whereas for the *N*-substituted compounds the *O*-amide results [(2) and (3)]. With *N*-thiobenzoylpiperidine, the *O*-amide product interacts further with any excess of mercury(II) ions present, as in (4). Tertiary *O*-amides are known [10,11] to form stable complexes with mercury(II)



ions. The subsequent hydrogen ion catalysed hydrolysis of the nitrile and *O*-amide products is very slow under the conditions used here, and mercury(II) ions are known not to catalyse such hydrolyses.[12]

The hydrogen ion catalysed hydrolysis of primary *S*-amides leads initially to a mixture of the *O*-amide and the thiol acid, the necessary conditions being such that these products then hydrolyse further in the reaction mixtures to the *O*-carboxylic acid.[6,13] It is clear that the acid Hg^{2+} distinguishes more than does H^+ between the sulphur and nitrogen sites of an *S*-amide, loss of sulphur being dominant in the present reactions. Nitriles have sometimes been reported to arise from *S*-amides, but normally under alkaline conditions.[12] The reason for the formation of nitrile from thiobenz-

[10] W. E. Bull, S. K. Madan, and J. F. Willis, *Inorg. Chem.*, 1963, **2**, 303.
[11] I. Baxter and G. A. Swan, *J. Chem. Soc.*, 1965, 3011.
[12] 'The Chemistry of Amides,' ed. J. Zabicky, Interscience, London, 1970.
[13] A. J. Hall and D. P. N. Satchell, *Chem. and Ind.*, 1974, 527.

amide in the present system, compared with the formation of *O*-amide when the sulphur atom is lost under the influence of hydrogen ions only, is discussed below. Given the exclusive loss of sulphur for thiobenzamide, the production of the *O*-amides from the *N*-substituted *S*-amides is, of course, expected since the formation of the nitrile in these cases would be very difficult.

Kinetic Behaviour and Reaction Mechanism for Thiobenzamide.—The Experimental section, Figure 1, and Table 1 reveal that (i) the observed decomposition of the initially formed 2 *S*-amide : 1 Hg^{2+} complex is a first order process in the presence of a sufficient, fixed excess of mercury(II) ions and at a constant value of $[H_3O^+]$, (ii) k_{obs} is proportional to $[Hg^{2+}]$ at any fixed value of

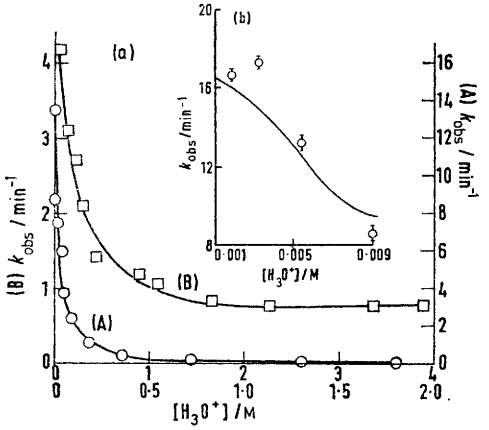


FIGURE 1 Effect of changes in $[H_3O^+]$ on k_{obs} for (a) thiobenzamide (A) and cyclohexylthiobenzamide (B) at 6·2° and (b) thiobenzamide at small values of $[H_3O^+]$. For conditions see Tables 1 and 2

$[H_3O^+]$, (iii) k_{obs} falls as $[H_3O^+]$ rises, at any fixed value of $[Hg^{2+}]$, passing from a region at low acidity where it is inversely proportional to $[H_3O^+]$, to a region at high acidity where it is effectively independent of $[H_3O^+]$.

The effect on k_{obs} of changes in $[H_3O^+]$ suggests that the latter is controlling one, or more, protonation equilibria relevant to the decomposition. Mercury(II) perchlorate is likely to be fully dissociated. The free mercury(II) ions will be hydrated (to an unknown extent) but it does not appear that an equilibrium like (5) could be significantly involved at the hydrogen ion concentrations used.[14] Also these concentrations were in-

$$[Hg(H_2O)_n]^{2+} + H_2O \rightleftharpoons [Hg(H_2O)_{n-1}OH]^+ + H_3O^+ \quad (5)$$

sufficient to lead to the significant protonation of any free *S*-amide.[6] It is likely therefore that the important protonation equilibria involve the *S*-amide–Hg^{2+} complex.

All the facts can be rationalised on the basis of reactions (6)—(16), in which the protonation equilibria are assumed to be much faster than the other steps.

[14] L. E. Sillen and A. E. Martell, Chem. Soc. Special Publication, No. 17, 1961.

For simplicity the equations are written without including molecules of hydration. Equilibria (6)—(11)

$$PhC(:S)NH_2 + Hg^{2+} \overset{fast}{\rightleftharpoons} [PhC(NH_2):S\rightarrow Hg]^{2+} \quad (6)$$

$$PhC(:S)NH_2 + [PhC(NH_2):S\rightarrow Hg]^{2+} \overset{fast}{\rightleftharpoons} \underset{(I)}{\{[PhC(NH_2):S]Hg\}^{2+}} \quad (7)$$

$$[PhC(NH_2):S\rightarrow Hg]^{2+} + H_2O \overset{fast;\ K_8}{\rightleftharpoons} [PhC(:NH)S-Hg]^+ + H_3O^+ \quad (8)$$

$$[PhC(:NH)S-Hg]^+ + PhC(:S)NH_2 \overset{k_9;\ fast}{\rightleftharpoons} \underset{(II)}{[PhC(:NH)S-Hg\leftarrow S:(NH_2)Ph]^+} \quad (9)$$

$$(I) + H_2O \overset{fast;\ K_{10}}{\rightleftharpoons} (II) + H_3O^+ \quad (10)$$

$$(II) + H_2O \overset{fast;\ K_{11}}{\rightleftharpoons} \underset{(III)}{[PhC(:NH)S]_2Hg} + H_3O^+ \quad (11)$$

$$(I) + Hg^{2+} \overset{k_{12};\ k_{-12}}{\rightleftharpoons} 2[PhC(NH_2):S\rightarrow Hg]^{2+} \quad (12)$$

$$(II) + Hg^{2+} \overset{k_{13};\ k_{-13}}{\rightleftharpoons} [PhC(NH_2):S\rightarrow Hg]^{2+} + [PhC(:NH)S-Hg]^+ \quad (13)$$

$$(III) + Hg^{2+} \overset{k_{14};\ k_{-14}}{\rightleftharpoons} 2[PhC(:NH)S-Hg]^+ \quad (14)$$

$$[PhC(:NH)S-Hg]^+ \overset{k_{15}}{\longrightarrow} PhC{\equiv}\overset{+}{N}H + HgS \quad (15)$$

$$PhC{\equiv}\overset{+}{N}H + H_2O \overset{fast}{\rightleftharpoons} PhCN + H_3O^+ \quad (16)$$

account for the rapid and effectively stoicheiometric formation of (I) [or of its deprotonated forms (II) and (III)]. These complexes are relatively stable in the absence of free mercury(II) ions. The ratios [(I)] : [(II)] : [(III)] will be influenced by $[H_3O^+]$, and equilibria (10) and (11) are assumed to be those which control the effect of $[H_3O^+]$ on k_{obs}. There is, in fact, some spectroscopic evidence for the formation of more than one 2 : 1 complex in that the extinction coefficient due to the complex decreases as the value of $[H_3O^+]$ rises. In any event it is difficult to explain the detailed dependence of k_{obs} on $[H_3O^+]$ unless three complexes are assumed to participate (see below). In the presence of free mercury(II) ions, 1 *S*-amide : 1 Hg^{2+} complexes can form *via* steps (12)—(14). The 1 : 1 complex decomposes irreversibly in step (15).

Reactions (6)—(16) can most easily be seen to lead to the observed reaction orders in [2 : 1 complex] and in mercury(II) ion if extreme conditions are considered for the hydrogen ion concentration. Thus when $[H_3O^+]$ is relatively very large, or very small, the only significant 2 : 1 complex species will be either (I) or (III). The

effective rate equation will then be either (17a or b).

$$-\mathrm{d}[2:1\ \text{complex}]/\mathrm{d}t = k_{12}[Hg^{2+}][(I)] \quad (17a)$$

$$-\mathrm{d}[2:1\ \text{complex}]/\mathrm{d}t = k_{14}[Hg^{2+}][(III)] \quad (17b)$$

Hence $-\mathrm{d}[2:1\ \text{complex}]/\mathrm{d}t = k_{obs}[2:1\ \text{complex}]$.

These equations correspond to the results obtained experimentally both so far as the reaction orders in $[Hg^{2+}]$ and in [2 : 1 complex] are concerned and with regard to the independence of k_{obs} of $[H_3O^+]$ under such conditions. This latter point is best seen from the results when $[H_3O^+]$ is large [Figure 1(a)]. The same trend is also evident when $[H_3O^+]$ is small but measurements in this region are less accurate (owing to the rapidity of the reaction) and we therefore quote fewer values [see Figure 1(b) and below].

It is assumed in writing equations (17) that the loss of $[PhC(:NH)S-Hg]^+$ *via* step (15) is much faster than its loss *via* the reversal of steps (14) and (13), so that, once formed, it in effect leads only to products. This is possible since (i) the rates of the reverse steps of equilibria (13) and (14) depend upon the product of two very small concentrations ($\lesssim 10^{-6}$M), and (ii) a value calculable for K_{10} suggests that K_8 will be sufficiently large for a significant fraction of the 1 : 1 complex to exist as $[PhC(:NH)S-Hg]^+$ even at high values of $[H_3O^+]$.

While k_{15} is assumed large enough to make the bimolecular reactions between the 2 : 1 complex and Hg^{2+} rate limiting, it must nevertheless also satisfy the relationship $k_{15} < k_9[PhCSNH_2]$ in the presence of free *S*-amide; otherwise, under conditions where the various monopositively charged complexes predominate, the observed 2 : 1 complex could never be formed.

The effect of varying $[H_3O^+]$, at a fixed value of $[Hg^{2+}]$, can be represented using reactions (6)—(16) as in equations (18)—(21). Because of the nature of the

$$-\mathrm{d}[2:1\ \text{complex}]_{total}/\mathrm{d}t = k_{obs}\{[(I)] + [(II)] + [(III)]\} \quad (18)$$

$$= \{k_{12}[(I)] + k_{13}[(II)] + k_{14}[(III)]\}[Hg^{2+}] \quad (19)$$

$$= k'_{12}[(I)] + k'_{13}[(II)] + k'_{14}[(III)] \quad (20)$$

$$\therefore\ k_{obs} = \frac{k'_{12}[H_3O^+]^2 + k'_{13}K_{10}[H_3O^+] + k'_{14}K_{10}K_{11}}{[H_3O^+]^2 + K_{10}[H_3O^+] + K_{10}K_{11}} \quad (21)$$

slow steps $k'_{12} < k'_{13} < k'_{14}$ is probable. Thus when $[H_3O^+]$ is small, equation (21) reduces to (22) or (23).

$$k_{obs} \simeq k'_{14}K_{11}/([H_3O^+] + K_{11}) \quad (22)$$

$$1/k_{obs} \simeq 1/k'_{14} + [H_3O^+]/k'_{14}K_{11} \quad (23)$$

When $[H_3O^+]$ is large, (21) becomes (24). Thus plots of

$$k_{obs} \simeq k'_{12} + k'_{13}K_{10}/[H_3O^+] \quad (24)$$

$1/k_{obs}$ against $[H_3O^+]$ and of k_{obs} against $1/[H_3O^+]$ at low and high acidities respectively, lead to values of k_{12}, k_{14}, $k_{13}K_{10}$, and K_{11}. These values, together with data for k_{obs} over the entire acidity range studied (*e.g.* Figure 1), can be used to compute the best values for all the constants. Our results for 6° are in Table 3. The continuous lines in Figures 1(a) and (b) are constructed using these values. The data for k_{obs} at 25° are sufficiently numerous for a partial analysis, and we calculate that for reaction (12) $E_a \simeq 14$ kcal mol^{-1} and $\Delta S^{\ddagger} \simeq -27$ cal mol^{-1} K^{-1} (Table 3).

TABLE 3

Derived equilibrium and kinetic parameters

For definitions of the various constants see text

(1) Thiobenzamide

(a) At 6·2°

$k_{12} = 28{\cdot}0$ l mol^{-1} min^{-1} $K_{10} = 0{\cdot}70$ mol l^{-1}

$k_{13} = 103$ l mol^{-1} min^{-1} $K_{11} = 0{\cdot}015$ mol l^{-1}

$k_{14} = 17{,}000$ l mol^{-1} min^{-1}

(b) At 26·5°

$k_{12} \simeq 170$ l mol^{-1} min^{-1}

For step (12) $E_a \simeq 14$ kcal mol^{-1} and $\Delta S^{\ddagger} \simeq -27$ cal mol^{-1} K^{-1}

(2) *N*-Cyclohexylthiobenzamide at 6·2°

$k_{12} = 525$ l mol^{-1} min^{-1} $K_{10} = 0{\cdot}11$ mol l^{-1}

$k_{13} = 7100$ l mol^{-1} min^{-1}

At $[H_3O^+] = 3{\cdot}9$M, $k_{obs} \simeq k'_{12}$. Hence for step (12) $E_a \simeq 13$ kcal mol^{-1} and $\Delta S^{\ddagger} \simeq -22$ cal mol^{-1} K^{-1}

Kinetics and Mechanism for the N-*Substituted* S-*Amides*.—For *N*-cyclohexylthiobenzamide the general

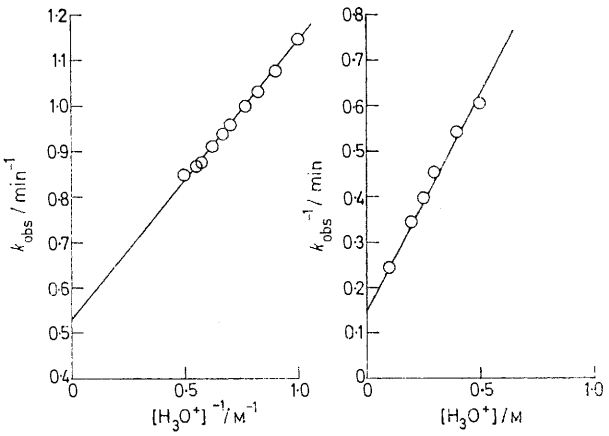


FIGURE 2 Plots of equations (23) and (24) for *N*-cyclohexylthiobenzamide

pattern of results [Table 2, Figure 1(a)(B)] is similar to that found for thiobenzamide. The greater reactivity of the cyclohexyl derivative prevented very low hydrogen ion concentrations being used and it is found that, for a fixed value of $[Hg^{2+}]$ and for varying values of $[H_3O^+]$, an analysis in terms of only two reactive forms of the 2 : 1 complex is sufficient to account for the data. If these forms are provisionally assumed to be the analogues of (I) and (II) then, using the relevant steps of the reaction scheme for thiobenzamide, k_{obs} can be shown to be given by equation (25). Appropriate plots (*e.g.* Figure 2) at high and low values of $[H_3O^+]$ lead to the three parameters (Table 3). The continuous curve in Figure 1(a)(B) is constructed using these constants.

$$k_{obs} = (k'_{12}[H_3O^+] + k'_{13}K_{10})/([H_3O^+] + K_{10}) \quad (25)$$

The reaction of *N*-thiobenzoylpiperidine was comparatively very slow. We have only qualitative results for this compound (Table 2).

Comparative Behaviour of the S-*Amides.*—The reactivity sequence for any given values of $[Hg^{2+}]$ and $[H_3O^+]$ is *N*-cyclohexylthiobenzamide > thiobenzamide ⩾ *N*-thiobenzoylpiperidine (Tables 1 and 2, Figure 1). Considering first the calculated parameters (Table 3) for thiobenzamide it is evident that (i) the values of k_{12}, k_{13}, and k_{14} are in a chemically sensible sequence, and (ii) the constants K_{10} and K_{11} are also sensibly related: the doubly charged complex would be expected to be a stronger proton donor than the singly charged species. Our analysis is therefore not only compatible with the overall kinetic behaviour, it leads to a chemically self-consistent set of derived parameters.

If we now compare the results for thiobenzamide with those for the cyclohexyl derivative we find only one equilibrium constant is detected for the latter compound. The value of this constant lies between those deduced for thiobenzamide (Table 3). Since the cyclohexyl derivative will be expected to be the more basic of the two compounds in the protonation equilibria [15] envisaged, it follows that the single constant detected for *N*-cyclohexylthiobenzamide probably refers to equilibrium (10) rather than (11). This has been assumed in writing equation (25). As explained above, equilibrium (11) was probably not detected for the cyclohexyl compound because work at low hydrogen ion concentrations was impracticable. The values of k_{12} and k_{13} are found to be (considerably) larger for the cyclohexyl derivative than for thiobenzamide. This is certainly a result in the right direction: the alkyl groups will repel electrons towards the sulphur atoms and so render attack by Hg^{2+} easier. The factor of *ca.* 70 between the two values of k_{13} seems, however, surprisingly large. It is possible that our value of k_{13} for the cyclohexyl compound contains a contribution from the 'undetected' k_{14}. This value should therefore be treated with caution. On the whole, nevertheless, the results for the cyclohexyl derivative are nicely compatible with those for thiobenzamide and the similar values obtained for the Arrhenius parameters of step (12) for the two compounds supports our choice of steps (12) and (13) as the important ones for the cyclohexyl derivative.

The results for *N*-thiobenzoylpiperidine are also understandable. The essential facts here are the rapid formation of the 2 : 1 complex and its comparatively very slow disappearance. Examination of reaction scheme (6)—(16) reveals that it requires simplification and modification for an *S*-amide which cannot lose protons. A possible revised scheme is (26)—(29). It seems unlikely that species (IV) would lose HgS directly (to give $PhC^{+}{=}\overset{+}{N}R_2$) and the displacement of HgS by water is probable, (28). This will make the mechanism of the metal promoted reaction more analogous to that of the simple hydrogen ion catalysed hydrolysis of *S*-amides,[6] thus accounting for the relatively slow rates observed for *N*-thiobenzoylpiperidine. For the *N*-cyclohexyl derivative, where the *O*-amide is also the final product, deprotonation of the 2 : 1 and 1 : 1 complexes can nevertheless still take place and it is only in the final

$$2PhC(:S)NR_2 + Hg^{2+} \overset{\text{fast}}{\rightleftharpoons} \{[PhC(:S)NR_2]_2Hg\}^{2+} \quad (26)$$

$$\{[PhC(:S)NR_2]_2Hg\}^{2+} + Hg^{2+} \rightleftharpoons 2[PhC(NR_2){:}S{\rightarrow}Hg]^{2+} \quad (27)$$
(IV)

$$PhC(:\overset{+}{N}R_2)S{-}Hg^{+} + H_2O \longrightarrow PhC(:NR_2)\overset{+}{O}H_2 + HgS \quad (28)$$
(IV)

$$PhC(:\overset{+}{N}R_2)\overset{+}{O}H_2 + 2H_2O \overset{\text{fast}}{\longrightarrow} PhCONR_2 + 2H_3O^+ \quad (29)$$

step of reactions (6)—(16) that any change is required. This could be along the lines of (30), a process likely to be rapid.

$$PhC{\equiv}\overset{+}{N}R + 2H_2O \longrightarrow PhC(:NR)OH + H_3O^+ \rightleftharpoons PhCONHR + H_3O^+ \quad (30)$$

The proposed slow steps of the thiobenzamide and *N*-cyclohexylthiobenzamide reactions are bimolecular reactions involving two doubly positively charged ions. The rates of such steps would be expected to vary greatly with ionic strength, at least in the region where the Debye–Hückel limiting law applies. It is unfortunately difficult to test this point with the present systems owing to the high ionic strengths resulting from the added perchloric acid. Indeed ionic activity coefficients would be expected to be approximately independent of ionic strength in the concentration region used in this work.

Relationship to Previous Work.—Previous kinetic studies [3,4,16] have been largely qualitative, have used thioacetamide, have involved heterogeneous conditions, and have not properly identified the final products. It is therefore difficult to draw any firm conclusions from these studies, but two points which emerge are (i) that complexes between the *S*-amide and Hg^{2+} are somehow involved, and (ii) the rate of formation of mercury(II) sulphide is retarded by increases in $[H_3O^+]$. Our results thus confirm, rationalise, and amplify these conclusions. Previous work involved either acetate or chloride as the counter ions. It is likely that the mechanism will be even more complicated in such systems since mercury(II) acetate and chloride are incompletely dissociated even at low concentrations. Further equilibria involving the association of Cl^- or AcO^- with the 2 : 1 and 1 : 1 *S*-amide–Hg^{2+} complexes will almost certainly have kinetic consequences. Probably, however, the essential mechanism will be similar to that revealed by the present work. The decelerating

[15] D. D. Perrin, 'The Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

[16] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1960, **82**, 4169.

effect of the addition of a large excess of *S*-amide observed by Swift *et al.*[3] could be due both to the formation of 4 *S*-amide : 1 mercury complexes, for which we have some evidence, and to the removal of the 1 : 1 complex *via* (7) before this latter species has a chance to decompose.

The probable reason that the hydrogen ion catalysed decomposition of primary *S*-amides leads to the *O*-amide,[13] rather than to the nitrile as found in our mercury promoted reactions, is that the sequence (31)

$$PhC(\overset{+}{:}SH)NH_2 + H_2O \rightleftharpoons PhC(:NH)SH + H_3O^+ \quad (31)$$

and (32) is much less favourable than (8) followed by

$$PhC(:NH)SH \longrightarrow PhC{\equiv}\overset{+}{N}H + HS^- \quad (32)$$

(15), so that the displacement of SH by H_2O predominates [reaction (33)].

$$PhC(\overset{+}{:}SH)NH_2 + H_2O \rightleftharpoons PhC(SH)(^+OH_2)NH_2 \longrightarrow PhC(\overset{+}{:}OH)NH_2 + H_2S \quad (33)$$

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