Kinetics and Mechanism of the Thallium(III) Ion Promoted Decomposition of Thiobenzamides in Aqueous Solution

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In aqueous solution at 25 °C thallium(I) ions do not detectably accelerate the decomposition of *S*-amides whereas thallium(III) ions bring about a rapid reaction. With thiobenzamide the organic product is benzonitrile, whereas with *N*-cyclohexylthiobenzamide and *N*-thiobenzoylpiperidine it is the corresponding *O*-amide. Spectroscopic and kinetic examination shows that all three *S*-amides form complexes with thallium(III) ions both rapidly and stoicheiometrically. With the thallium ions in deficit, thiobenzamide forms a 2 : 1 *S*-amide–Tl^{3+} complex which is converted into a 1 : 1 complex as [Tl^{3+}] is raised. *N*-cyclohexylthiobenzamide and *N*-thiobenzoylpiperidine form 4 : 1 *S*-amide–Tl^{3+} complexes with a deficit of thallium ions, these complexes being converted into complexes of lower stoicheiometry as the thallium concentration is increased. In the presence of a large excess of thallium ions the predominant species is the 1 : 1 complex. The decomposition of the *S*-amides to benzonitrile (or *O*-amide) proceeds *via* the complexes, the 1 : 1 complexes being much less reactive than the 2 : 1 complexes. At high thallium(III) ion concentrations the rate of decomposition is inversely related to [Tl^{3+}] since increase in [Tl^{3+}] proportionately decreases the small equilibrium concentration of 2 : 1 complex. Reaction mixtures normally contained [H_3O^+] $\gtrsim$ 0.2M to suppress the dissociation of protons from water molecules bound to the thallium ions. Changes in [H_3O^+] above 0.2M have little effect on the rate which, however, exhibits a powerful negative ionic strength effect. The prior dissociation of protons from the various complexes is unimportant in determining the reaction rate and a mechanism of decomposition is suggested. Some differences between the thallium promoted reactions and those promoted by other soft metal ions are pointed out. From a preparative viewpoint thallium(III) and gold(III) salts are likely to be better promoters of the decomposition of *NN*-disubstituted *S*-amides than are salts of mercury(II) or silver.

We have recently described the products, kinetics, and mechanisms found for a number of soft metal ion promoted decompositions of *S*-amides † in aqueous solution.[1] We report now a study of the thallium ion promoted reaction. Systems involving thallium ions and *S*-amides have not been much studied, although it is known that complexes can be formed with thiourea.[2] Thallium(III) salts have been used to cleave other thio-compounds (*e.g.* thioacetals [3]) and Tl^{3+} appears qualitatively to be one of the softest metal ions.[4]

Thallium(III) ions are hydrated in aqueous solution

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† For clarity we use *S*-amide ≡ thioamide and *O*-amide ≡ amide.

[1] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 1351, and earlier papers.

[2] ' Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon, New York, 1972, vol. 1, pp. 1161, 1149.

[3] T. L. Ho and C. M. Wong, *Canad. J. Chem.*, 1972, **50**, 3740.

[4] S. Arhland, *Structure and Bonding*, 1966, **1**, 207; 1968, **5**, 118.

and the dissociation constants for reactions (1) and (2) are known:[5] $K_1 \simeq 0.07$ and $K_2 \simeq 0.03\text{M}$. To simplify the systems, the majority of our experiments were conducted with $[H_3O^+] \gtrsim 0.2\text{M}$ to suppress largely this dissociation. The *S*-amides are negligibly protonated at the acidities used.[6]

$$[\mathrm{Tl(H_2O)}_n]^{3+} + \mathrm{H_2O} \xrightleftharpoons{K_1} [\mathrm{Tl(H_2O)}_{n-1}\mathrm{OH}]^{2+} + \mathrm{H_3O^+} \quad (1)$$

$$[\mathrm{Tl(H_2O)}_{n-1}\mathrm{OH}]^{2+} + \mathrm{H_2O} \xrightleftharpoons{K_2} [\mathrm{Tl(H_2O)}_{n-2}(\mathrm{OH})_2]^{+} + \mathrm{H_3O^+} \quad (2)$$

EXPERIMENTAL

Materials.—Thiobenzamide, *N*-cyclohexylthiobenzamide, thiobenzoylpiperidine, and their *O*-analogues were previous samples,[1] as was benzonitrile. Perchloric acid, sodium perchlorate, diethyl ether, ethanol, and carbon tetrachloride were of AnalaR grade; thallium(I) and thallium(III) nitrates were B.D.H. reagent grade materials.

Formation of Complexes.—As with mercury(II) and silver ions,[7,8] thiobenzamides readily form complexes with thallium(III) ions in aqueous solution. For example, thiobenzamide has an absorption band centred on 290 nm (ε 8 200) which is shifted to slightly shorter wavelengths and intensified on addition of thallium(III) ions. Experiments along the lines described by Harvey and Manning,[9] in which measurements were made of the optical densities (at 290 nm) of a series of solutions of fixed ($5 \times 10^{-5}\text{M}$) thiobenzamide concentration but of increasing (0—$5 \times 10^{-4}\text{M}$) thallium ion concentration, showed that thiobenzamide is rapidly and quantitatively complexed by the thallium ions, forming, at low thallium concentrations, a 2 : 1 *S*-amide–$\mathrm{Tl^{3+}}$ complex, which is converted into a 1 : 1 complex (ε_{290} 15 000) when $[\mathrm{Tl^{3+}}] > [S\text{-amide}]$. Similar experiments with *N*-cyclohexylthiobenzamide (ε_{278} 8 300) indicated quantitative formation of a 4 : 1 *S*-amide–$\mathrm{Tl^{3+}}$ complex (ε_{275} 12 500) when $[\mathrm{Tl^{3+}}] \ll [S\text{-amide}]$, which is converted into a complex (or complexes) of lower stoicheiometry as $[\mathrm{Tl^{3+}}]$ is increased. When $[\mathrm{Tl^{3+}}] \gg [S\text{-amide}]$ the 1 : 1 complex is probably dominant (ε_{275} 11 200). Results for *N*-thiobenzoylpiperidine (ε_{278} 12 600) were similar, the 4 : 1 and 1 : 1 complexes having ε_{265} 15 000 and 14 000, respectively. As indicated in later sections, the *S*-amide–$\mathrm{Tl^{3+}}$ complexes decompose irreversibly with loss of sulphur. This decomposition is sufficiently fast when $[\mathrm{Tl^{3+}}] \gtrsim 5 \times 10^{-4}\text{M}$ to render slightly inaccurate initial optical density measurements made using a conventional recording spectrophotometer. Therefore the optical density measurements referring to complex formation were made with a Durrum–Gibson stopped-flow spectrophotometer calibrated against a Unicam SP 800 instrument. Use of the stopped-flow technique enabled the optical densities referring to the very rapidly formed complexes to be determined with negligible errors from the subsequent decomposition of the complexes. (The stopped-flow technique did not, however, permit any study of the kinetics of complex formation, this being too rapid.) The presence of various concentrations ($\gtrsim 0.2\text{M}$) of hydrogen ions had little effect on the spectra of the complexes.

Products.—Preparative scale experiments, using concentration conditions which simulated as far as possible those of the kinetic experiments, showed that the final organic product from thiobenzamide is benzonitrile, whereas that from the other *S*-amides is the corresponding *O*-amide. All these products were isolated in 82—98% yield and the spectral changes noted during the kinetic experiments indicated that the reactions are effectively quantitative. Also isolated from all the preparative scale experiments was free sulphur. This suggests that the overall processes correspond to equations (3)—(5). Thallium(III) sulphide is known to be unstable and to lead to thallium(I) ions and free sulphur.[2] We find that thallium(I) ions themselves cause negligible decomposition of thioamides in comparison with thallium(III) ions.

$$\mathrm{PhCSNH_2} + \mathrm{Tl^{3+}} + 2\mathrm{H_2O} \longrightarrow \mathrm{PhCN} + 2\mathrm{H_3O^+} + \mathrm{Tl^+} + \mathrm{S} \quad (3)$$

$$\mathrm{PhCSNHC_6H_{11}} + \mathrm{Tl^{3+}} + 3\mathrm{H_2O} \longrightarrow \mathrm{PhCONHC_6H_{11}} + 2\mathrm{H_3O^+} + \mathrm{Tl^+} + \mathrm{S} \quad (4)$$

$$\mathrm{PhCSN[CH_2]_5} + \mathrm{Tl^{3+}} + 3\mathrm{H_2O} \longrightarrow \mathrm{PhCON[CH_2]_5} + 2\mathrm{H_3O^+} + \mathrm{Tl^+} + \mathrm{S} \quad (5)$$

Kinetic Arrangements.—The decomposition of the *S*-amides was studied kinetically. The arrangements followed lines used in our previous studies[1] and employed a Unicam SP 800 recording spectrophotometer. All the reaction components, except the *S*-amide, were thermostatted in the spectrophotometer cell (quartz, 10 mm path, *ca.* 3 ml capacity) and reactions were initiated by the addition of a small aliquot portion of a stock solution of the *S*-amide in ethanol. The final mixture contained 2% (v/v) ethanol. As described above, the *S*-amide is rapidly and quantitatively converted into a complex with the thallium(III) ions; the subsequent optical density changes correspond to the decomposition of this complex according to the overall equations (3)—(5). The disappearance of complex was monitored at 290, 275, and 265 nm, respectively, for thiobenzamide, *N*-cyclohexylthiobenzamide and *N*-thiobenzoylpiperidine. For thiobenzoylpiperidine the loss of complex follows second-order kinetics and k_{obs}, the observed second-order rate constant, was calculated from the equation $ak_{\text{obs}}t = x/(a - x)$, in which a represents the initial concentration of complex and x the amount consumed after time t. Values of k_{obs} were reproducible to within $\pm 10\%$. For the other *S*-amides the apparent reaction order in complex lies between one and two. Our method of calculation of rate constants for these compounds is discussed below. The detailed results of all the kinetic experiments are in Tables 1—3. Systematic variation of the *S*-amide, thallium(III) ion, hydrogen ion, and added salt concentrations was examined. In these experiments the thallium(III) ion concentration was normally at least 10-fold greater than that of the initial *S*-amide; this ensured that the observed complex was essentially the 1 : 1 species and also rendered the decomposition slow enough for the initial optical density measurements to be made accurately with the SP 800 instrument (see above). Reaction mixtures remained homogeneous throughout the kinetic runs but a

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

[6] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1974, 1077.

[7] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778.

[8] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 1273.

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

precipitate of sulphur was eventually formed after long periods. This result is compatible with the results of the preparative scale experiments described above. Trial kinetic experiments using thallium(I) ions showed that, again in agreement with preparative experiments, they lead to a negligible decomposition of the *S*-amides. All kinetic experiments were performed at 25 °C.

RESULTS AND DISCUSSION

(i) *Thiobenzamide*.—The predominant *S*-amide species in solution prior to decomposition to benzonitrile is, under the concentration conditions of the kinetic experiments, the 1 : 1 *S*-amide–Tl^{3+} complex (C_1). This species will be in equilibrium with relatively small amounts of free *S*-amide and of the 2 : 1 *S*-amide–Tl^{3+} complex (C_2) (see Experimental section). The disappearance of the 1 : 1 complex is the process observed kinetically. Use of the first-order rate equation $2.3 \log[C_1]_0/[C_1]_t = k_{obs}t$ showed that it is obeyed well only for about the first 25% of the reaction, the reaction thereafter slowing too much. Use of the second-order rate equation gives, however, no better a fit, and the loss of 1 : 1 complex corresponds to a fractional order of between 1 and 2. This type of order is inconvenient so far as the use of an integrated rate equation is concerned, but it has proved sufficient for our present purposes to calculate the apparent first-order rate constant, $k_{obs}{}^a$, corresponding to the initial stages of the reaction. The values of $k_{obs}{}^a$ given in Table 1 are based upon initial slopes and are averages of two, or more, experiments; the values are reliable to within ±10%.

TABLE 1

Reaction of thiobenzamide with thallium(III) ions at 25 °C

[*S*-amide]$_0$ *ca.* 10^{-4}M (unless stated otherwise); solvent 2% v/v ethanol–water, $k_{obs}{}^a$ = apparent first-order rate constant (see text)

(i) Effect of [Tl^{3+}] ([$HClO_4$]$_{stoich}$ 1.06M)						
$10^3[Tl^{3+}]$/M	0.5	1.0	2.0	4.0	8.0	
$10^2k_{obs}{}^a$/s^{-1}	2.72	1.38	0.96	0.59	0.41	
(ii) Effect of [$HClO_4$]$_{stoich}$						
(a) $10^3[Tl^{3+}]$ 1.0M						
[$HClO_4$]/M	0.098	0.20	0.49	0.98	1.96	2.94
$10^2k_{obs}{}^a$/s^{-1}	1.44	1.39	1.38	1.37	1.31	1.07
(b) $10^2[Tl^{3+}]$ 1.0M						
[$HClO_4$]/M	0.98	1.96	2.94	3.92		
$10^3k_{obs}{}^a$/s^{-1}	2.65	1.62	1.52	1.22		
(iii) Effect of [$NaClO_4$] ([$HClO_4$]$_{stoich}$ 0.98M)						
(a) $10^3[Tl^{3+}]$ 1.0 M						
[$NaClO_4$]/M	0	1.0	2.0	3.0		
$10^2k_{obs}{}^a$/s^{-1}	1.37	1.29	1.24	1.01		
(b) $10^2[Tl^{3+}]$ 1.0M						
[$NaClO_4$]/M	0	1.0	2.0	3.0		
$10^3k_{obs}{}^a$/s^{-1}	2.65	1.86	1.38	1.17		
(iv) Effect of [*S*-amide]$_0$ ($10^3[Tl^{3+}]$ 1.0M; [$HClO_4$]$_{stoich}$ 0.98 M)						
10^5[*S*-amide]$_0$/M	2.5	5.0	7.5	10.0		
$10^3k_{obs}{}^a$/s^{-1}	6.90	9.10	11.6	13.7		

Table 1 shows that (*a*) at fixed hydrogen ion and initial *S*-amide concentrations, $k_{obs}{}^a$ falls as [Tl^{3+}] rises and a plot of $k_{obs}{}^a$ against 1/[Tl^{3+}] is rectilinear with an intercept on the $k_{obs}{}^a$ axis (Figure 1); (*b*) at fixed hydrogen ion and thallium ion concentrations, $k_{obs}{}^a$ increases as [*S*-amide]$_0$ increases and a plot of $k_{obs}{}^a$ against [*S*-amide]$_0$ is also rectilinear with an intercept on the $k_{obs}{}^a$ axis (Figure 1); (*c*) at fixed thallium ion and initial *S*-amide concentrations, $k_{obs}{}^a$ falls as [$HClO_4$]$_{stoich}$ is increased, but similar effects are produced by adding sodium perchlorate in place of perchloric acid (Figure 2).

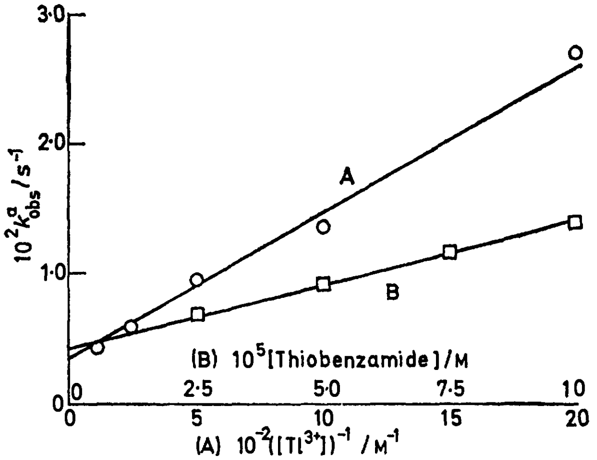


FIGURE 1 Tests of equation (11) for thiobenzamide: A, effect of [Tl^{3+}] when [$HClO_4$]$_{stoich}$ = 1.06M and [*S*-amide]$_0$ = 10^{-4}M; B, effect of [*S*-amide]$_0$ when [Tl^{3+}] = 10^{-3}M and [$HClO_4$]$_{stoich}$ = 0.98M

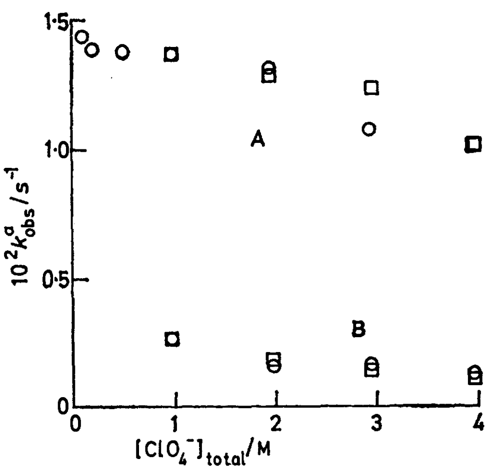
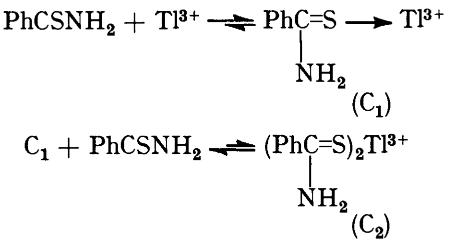


FIGURE 2 Effects on $k_{obs}{}^a$ of added perchloric acid or sodium perchlorate; [*S*-amide]$_0$ 10^{-4}M; A, [Tl^{3+}] 10^{-3}M; B, [Tl^{3+}] 10^{-2}M. For ○, perchlorate added as $HClO_4$. For □, perchlorate added as $HClO_4$ (0.98M) plus $NaClO_4$ (0.0—3.0M)

We assume therefore that this fall in $k_{obs}{}^a$ arises from a salt effect rather than from the effect of changes in [H_3O^+] on a kinetically important protonation equilibrium.

These facts can be accounted for by the outline mechanism (6)—(9), from which water molecules of hydration have been omitted for convenience. Since [C_1] ≫ [C_2], and C_1 and C_2 are in rapid equilibrium, equation (10) applies. In equation (12) $k_{obs}{}^a$ is the



$$PhCSNH_2 + Tl^{3+} \rightleftharpoons \underset{\substack{| \\ NH_2}}{PhC{=}S} \longrightarrow Tl^{3+} \quad (C_1) \qquad K_1\text{, fast} \qquad (6)$$

$$C_1 + PhCSNH_2 \rightleftharpoons (\underset{\substack{| \\ NH_2}}{PhC{=}S})_2Tl^{3+} \quad (C_2) \qquad K_2\text{, fast} \qquad (7)$$

$$C_1 \xrightarrow{+H_2O} \text{Products} \qquad k_1\text{, slow} \qquad (8)$$

$$C_2 \xrightarrow{+H_2O} \text{Products} \qquad k_2\text{, slow} \qquad (9)$$

$$\text{Rate} = -d[C_1]/dt = k_1[C_1] + k_2[C_2] \qquad (10)$$

$$\text{But} \quad \frac{K_1}{K_2} = \frac{[C_1]^2}{[C_2]}\frac{1}{[Tl^{3+}]} \text{ or } [C_2] = K[C_1]^2/[Tl^{3+}]$$

$$\therefore \quad -d[C_1]/dt = k_1[C_1] + k_2K[C_1]^2/[Tl^{3+}]$$
$$= (k_1 + k_2K[C_1]/[Tl^{3+}])[C_1] \qquad (11)$$

$$\text{or} \qquad -d[C_1]/dt = k_{obs}{}^a[C_1] \qquad (12)$$

apparent first-order rate constant for the initial period of the reaction where $[C_1] \simeq [S\text{-amide}]_0$. If this mechanism is correct plots of $k_{obs}{}^a$ against $1/[Tl^{3+}]$, or against $[S\text{-amide}]_0$, should provide straight lines with a common intercept, k_1. Figure 1 shows this to be (approximately) the case and the slopes of the two plots lead in fact to similar values for k_2K. We find that $k_1 = (3.85 \pm 0.25) \times 10^{-3}$ s^{-1} and $k_2K = k_2K_2/K_1 = 0.106 \pm 0.004$ s^{-1}. The negative salt effect found on increasing [$HClO_4$] or [$NaClO_4$] may arise partly from the progressive reduction of K_2/K_1 at high ionic strengths, since the 1 : 1 complex will probably be the more polar of the two. Discussion of the details of steps (8) and (9) is deferred.

(ii) N-*Cyclohexylthiobenzamide*.—The product here is the *O*-amide, but otherwise the pattern of results obtained is similar to that found with thiobenzamide; the results were treated in the same way and an analogous outline mechanism can apply. We find $k_1 = (0.60 \pm 0.20) \times 10^{-3}$ s^{-1} and $k_2K_2/K_1 = 0.098 \pm 0.004$ s^{-1} (Figure 3). Values of $k_{obs}{}^a$ are in Table 2.

TABLE 2

Reaction of *N*-cyclohexylthiobenzamide with thallium(III) ions at 25 °C

$[S\text{-amide}]_0$ *ca.* 1×10^{-4}M (unless stated otherwise); solvent 2% v/v ethanol–water; $k_{obs}{}^a$ = apparent first-order rate constant (see text)

(i) Effect of [Tl^{3+}] ([$HClO_4$]$_{stoich}$ 0.98M)

$10^3[Tl^{3+}]$/M	1.0	1.5	2.0	3.0	4.0	6.0	8.0
$10^3k_{obs}{}^a$/s^{-1}	10.7	7.57	5.51	3.86	3.54	2.05	1.52

(ii) Effect of [$HClO_4$]$_{stoich}$

(a) $10^3[Tl^{3+}]$ 1.0M

[$HClO_4$]/M	0.49	0.98	1.96	2.94	3.92
$10^3k_{obs}{}^a$/s^{-1}	11.3	10.7	8.69	6.44	3.68

(b) $10^2[Tl^{3+}]$ 1.0M

[$HClO_4$]/M	0.49	0.98	1.96	2.94
$10^3k_{obs}{}^a$/s^{-1}	1.40	1.30	1.17	0.83

(iii) Effect of $[S\text{-amide}]_0$ ($10^3[Tl^{3+}]$ 1.0M; [$HClO_4$]$_{stoich}$ 0.98M)

$10^4[S\text{-amide}]_0$/M	1.00	1.25	1.50
$10^3k_{obs}{}^a$/s^{-1}	10.7	13.3	15.6

(iii) N-*Thiobenzoylpiperidine*.—As for the other *N*-substituted *S*-amide the product here is the *O*-amide. This time, however, the kinetic results for loss of the *S*-amide–Tl^{3+} complex display good second-order behaviour and a plot of k_{obs} (Table 3) against $1/[Tl^{3+}]$ is rectilinear and passes through the origin (Figure 4). These results are easily interpreted on the basis of our mechanism (6)—(9) for thiobenzamide. They imply that for *N*-thiobenzoylpiperidine only the 2 : 1 complex contributes significantly to the decomposition; equation (11) then reduces to (13), which is in keeping with the

$$-d[C_1]/dt = k_2K[C_1]^2/[Tl^{3+}] \qquad (13)$$
$$= k_{obs}[C_1]^2 \qquad (14)$$

observed behaviour. Our value for k_2K_2/K_1 is 0.075 ± 0.003 s^{-1}.

TABLE 3

Reaction of *N*-thiobenzoylpiperidine with thallium(III) ions at 25 °C

$[S\text{-amide}]_0$ *ca.* 10^{-4}M (unless stated otherwise); solvent 2% v/v ethanol–water; k_{obs} = observed second-order rate constant

(i) Effect of [Tl^{3+}]

(a) [$HClO_4$]$_{stoich}$ 0.98M

$10^3[Tl^{3+}]$/M	1.0	1.5	2.0	3.0	6.0	8.0	10.0
k_{obs}/l mol^{-1} s^{-1}	74	48	38	23	13	8.7	8.5

(b) [$HClO_4$]$_{stoich}$ 0.20M

$10^3[Tl^{3+}]$/M	1.5	2.0	3.0	4.0
k_{obs}/l mol^{-1} s^{-1}	84	64	42	34

(ii) Effect of [$HClO_4$]$_{stoich}$ ($10^3[Tl^{3+}]$ 1.0M)

[$HClO_4$]/M	0.49	0.98	1.96	2.94	3.92	4.90
k_{obs}/l mol^{-1} s^{-1}	79	74	55	37	24	14

(iii) Effect of [$NaClO_4$] ($10^3[Tl^{3+}]$ 1.0M; [$HClO_4$]$_{stoich}$ = 0.98M)

[$NaClO_4$]/M	0	0.5	1.0	2.0	3.0
k_{obs}/l mol^{-1} s^{-1}	74	64	57	42	30

(iv) Effect of $[S\text{-amide}]_0$ ($10^3[Tl^{3+}]$ 1.0M; [$HClO_4$]$_{stoich}$ 0.98M)

$10^5[S\text{-amide}]_0$/M	4.0	7.5	10	15
k_{obs}/l mol^{-1} s^{-1}	80	74	74	83

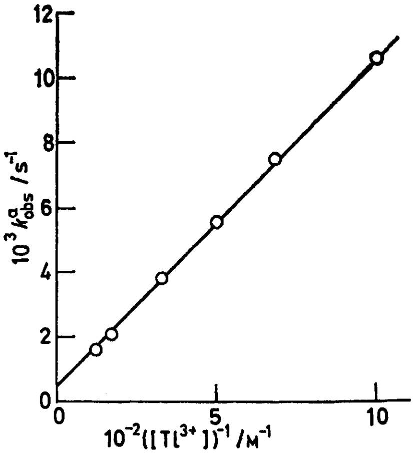


FIGURE 3 Plot of equation (11) for *N*-cyclohexylthiobenzamide; $[S\text{-amide}]_0$ 10^{-4}M; [$HClO_4$]$_{stoich}$ 0.98M

(iv) *Detailed Mechanism*.—As noted above, thallium(III) ions are hydrated in aqueous solution (to an unknown extent) and at least two of the water protons are dissociated if the ambient hydrogen ion concentration is sufficiently small [equations (1) and (2)]. In nearly all our reaction mixtures equilibria (1) and (2) will lie far to the left, so that any alterations made in [H_3O^+] will not significantly alter the [$Tl(H_2O)_n$]$^{3+}$ concentration, but will materially affect the very small equilibrium concentrations of [$Tl(H_2O)_{n-1}OH$]$^{2+}$ and [$Tl(H_2O)_{n-2}(OH)_2$]$^+$. Nothing is known about the acid dissociation constants of species such as [$Tl(PhCSNR_2)(H_2O)_{n-1}$]$^{2+}$ and [$Tl(PhCSNR_2)_2(H_2O)_{n-2}$]$^{3+}$, but it is perhaps fair to assume that, at the relatively high hydrogen ion concentrations always used here, an analogous situation will apply for the dissociation of their water protons. The fact that the changes in [$HClO_4$] studied produce effects on k_{obs} little different from those produced by $NaClO_4$ therefore indicates that the dissociation of the water protons is inessential for the decomposition reaction and that the contribution from species such as [$Tl(PhCSNR_2)_2(H_2O)_{n-3}OH$]$^{2+}$ is negligible.

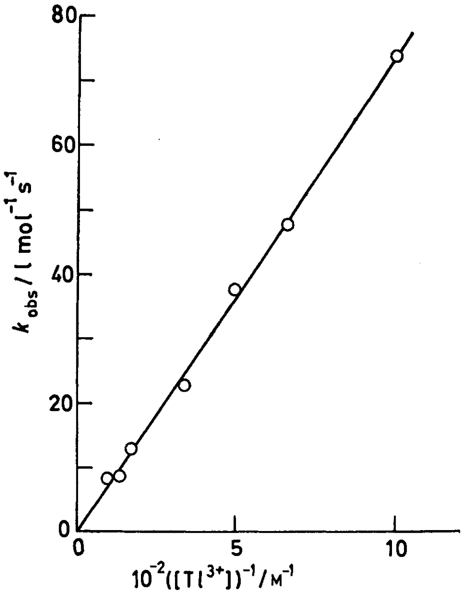
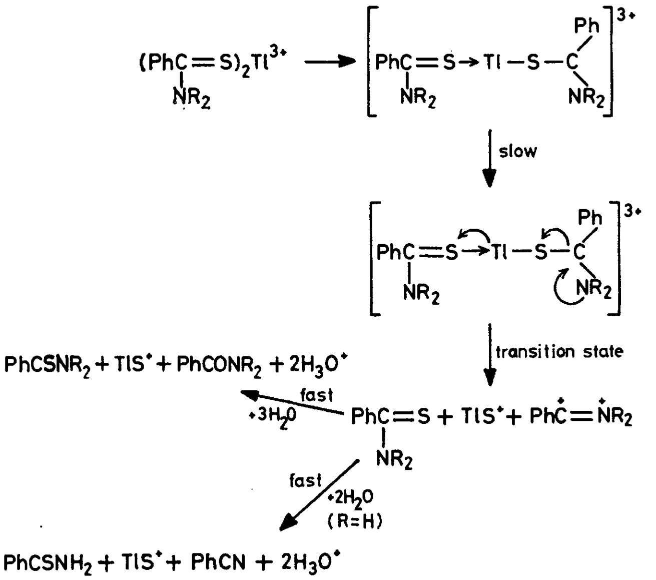


FIGURE 4 Plot of equation (13) for *N*-thiobenzoylpiperidine; [*S*-amide]$_0$ 10^{-4}M; [$HClO_4$]$_{stoich}$ 0.98M

Besides their water protons the 1 : 1 and 2 : 1 complexes of thiobenzamide and *N*-cyclohexylthiobenzamide also possess potentially ionisable N–H protons. Indeed the ionisation of the corresponding proton is very important in the mechanisms of the mercury(II) and silver ion promoted reactions[7,8] where *N*-thiobenzoylpiperidine, because it has no N–H protons to lose, reacts negligibly slowly in comparison with thiobenzamide and the *N*-cyclohexyl derivative. Two facts therefore point to the kinetic unimportance of the acid dissociation of the N–H proton in the thallium(III) reaction: (*a*) the similar rates found for all three *S*-amides, and (*b*) the absence of any marked effects attributable to changes in [H_3O^+].

In view of the foregoing discussion it is probable that the reactive complex is, indeed, a triply charged entity, as assumed in equations (6)—(9). The remaining questions about the mechanism concern (*a*) the details of the slow steps (8) and (9), and (*b*) the reason for the relatively great reactivity of the 2 : 1 in comparison with the 1 : 1 complexes. These questions are difficult to answer. We speculate that reaction (9) may proceed somewhat as shown in the Scheme. It may be that the presence of the second *S*-amide ligand facilitates the slow cleavage of the C–S bond of the first, since the presence of one soft ligand in a metal complex often renders the metal atom a much softer species.[10] However, in the mercury(II) ion promoted reaction it is only the 1 : 1 complex, and not the 2 : 1 complex, which leads to reaction, although the latter predominates in solution. There is clearly still much to learn about the factors which control the reactivity of the different types of complex. In the Scheme charge is appreciably dispersed in the transition state and this would be expected to lead to a lower rate at high ionic strength, as found. As noted above, the effect of ionic strength on the pre-equilibria (6) and (7) could work in the same direction.



SCHEME

Whilst the mechanisms with all the metal ions we have studied[1] have significant differences of detail, the thallium(III) ion promoted decomposition is generally more akin to the gold(III) promoted reaction than to those promoted by mercury(II), copper(II), and silver ions: with both gold and thallium the ionisation of the *S*-amide's N–H protons is unimportant kinetically and thiobenzoylpiperidine has a reactivity similar to that of thiobenzamide itself.

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[10] R. G. Pearson, *Science*, 1966, **151**, 172.