The Kinetics of the Soft Metal Ion Promoted Hydrolysis of Phenyl Isothiocyanates in Aqueous Solution. The Effects of Thallium(III) Ions and of Substituents

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In the Hg^{2^+} ion-promoted hydrolysis of RC_6H_4NCS a large increase in electron-release by R produces only a small increase in reaction rate. These substituent effects support the mechanism previously proposed. TI^{3^+} ions are surprisingly much (*ca.* 10^3 -fold) less effective in promoting the hydrolyses than are Hg^{2^+} ions, but show the same kinetic form and similar substituent effects. A similar mechanism is suggested. The low reactivity of TI^{3^+} ions, the different pattern of their activation parameters, and the greater dependence of the TI^{3^+} ion-promotion on ionic strength, all suggest that these ions form adducts with isothiocyanates with special difficulty; the comparable reactivity normally found for Hg^{2^+} and TI^{3^+} ions when promoting the decomposition of organosulphur compounds may require chelating substrates.

Our recent kinetic studies 1,2 show (i) that the hydrolysis of phenyl isothiocyanates in aqueous solution, eqn. (1), is

$$\begin{array}{c} \mathrm{RC}_{6}\mathrm{H}_{4}\mathrm{NCS} \,+\,\mathrm{H}_{2}\mathrm{O} \longrightarrow [\mathrm{RC}_{6}\mathrm{H}_{4}\mathrm{NHCOSH}] \longrightarrow \\ \mathrm{RC}_{6}\mathrm{H}_{4}\mathrm{NH}_{2} \,+\, [\mathrm{COS}](\xrightarrow{\mathrm{H}_{2}\mathrm{O}}\mathrm{H}_{2}\mathrm{S} \,+\,\mathrm{CO}_{2}) \quad (1) \end{array}$$

significantly catalysed only at relatively high (>8.0 mol dm⁻³) concentrations of hydrogen ions and (ii) that low concentrations of Ag⁺ and of mercury(II) ions effectively promote the hydrolysis of *p*-nitrophenyl isothiocyanate. We report now for the first time on the kinetics of the Tl³⁺ ion-promoted hydrolysis, and on the effects of substituents in the isothiocyanate on the rates of the Hg²⁺ and Tl³⁺ ion-promoted reactions.

Experimental

The materials were mostly previous samples.^{1,2} Thallium(III) nitrate was of AnalaR grade. In the Hg²⁺ ion-promotion the kinetics were studied essentially as before,² and the loss of isothiocyanate absorption was monitored at the absorption maximum. With Tl³⁺ ions it was necessary to maintain $[H_3O^+] > 0.2$ mol dm⁻³ to avoid precipitation of the metal hydroxide during these relatively slow runs.³ Otherwise the conditions were similar to those used with Hg²⁺ ions, and reaction was monitored in the same way.

Preparative experiments showed the organic product was in all cases the corresponding aniline. The absorbance changes during the runs showed that the products were formed in very high yield. The observed pseudo-first-order rate constants, k_{obs} , were reproducible to within $\pm 6\%$ with Hg²⁺ ions, and to within $\pm 12\%$ with Tl³⁺ ions. Reaction mixtures remained homogeneous throughout the runs. Our results, and the various concentrations and other conditions, are in the Tables and Figures. The spontaneous hydrolysis of the isothiocyanates was always negligible during Hg^{2+} ion promotion, and contributed little to the observed rates in the Tl^{3+} ion systems.

Results and Discussion

(i) Mercury(III) Ion Promotion .--- Our previous work² with p-nitrophenyl isothiocyanate showed the reaction to be firstorder in the isothiocyanate and Hg²⁺ ion concentrations, and to have $\Delta S^{\ddagger} = -58 \text{ J K}^{-1} \text{ mol}^{-1}$. Changes in $[H_3O^+]$ (up to 0.3 mol dm⁻³) had no effect on k_{obs} , and an increase in ionic strength led to a modest increase in k_{obs} . We proposed the mechanism given in eqns. (2)–(4) for which $k_{obs} = k_{Hg}K_{Hg}[Hg^2]$ ⁺] ≕ $k[Hg^{2+}]$ where k is the second-order constant. In the present work the hydrolysis of all the isothiocyanates used with Hg²⁺ ions (Table 1) also display a simple first-order dependence on $[Hg^{2+}]$ (see, e.g., Fig. 1). If the above mechanism is correct, changing the nature of R, under otherwise fixed conditions, is likely to have only a moderate effect on k since an increase in electron release should increase K_{Hg} but will probably decrease k_{Hg} . Our results (Tables 1 and 3) are in agreement with this prediction, and the small increase in k suggests that the effect on K_{Hg} is just dominant. (For the simple bimolecular reaction of glycine or OH⁻ ions with phenyl isothiocyanates⁴ a change from the p-NO₂ to the p-MeO derivative produces a decrease in the rate constant by a factor of ca. 20). If, as we propose, the slow step is an attack by water on II, then an ortho substituent might be expected to exhibit some steric hindrance because attack is likely to be in the molecular plane.⁵ The result for the o-Me group (Table 1) is therefore also in line with expectations from eqns. (2)-(4).

All the isothiocyanates used have similar activation parameters (Table 3), although ΔS^{\dagger} is significantly more negative for the *o*-Me derivative; this again is compatible with steric hindrance of the slow step. In all, our present results for Hg²⁺ ion-promotion are supportive of the mechanism previously proposed.²

$$\begin{array}{c} \operatorname{RC}_{6}\operatorname{H}_{4}\operatorname{NCS} + \operatorname{Hg}^{2+} & \xrightarrow{\operatorname{fast}} \operatorname{RC}_{6}\operatorname{H}_{4}\operatorname{NCS} \longrightarrow \operatorname{Hg}^{2+} & K_{\operatorname{Hg}} \\ I & II \end{array}$$
(2)

$$II + 2 H_2O \xrightarrow{\text{slow}} RC_6H_4N = C-S-Hg^+ + H_3O^+ \qquad k_{Hg}$$
(3)

$$RC_{6}H_{4}NH_{2} + HgS + CO_{2} + 2H_{3}O^{+} \xleftarrow{fast}{H_{2}O} RC_{6}H_{4}NHC - S - Hg^{+} + H_{3}O^{+}$$

$$\parallel O$$
(4)

 Table 1
 Rate constants for Hg²⁺ ion promotion^a

	T/°C	[Hg ²⁺]/10 ⁻³ mol dm ³	$\frac{k_{obs}}{s^{-1}}/10^{-3}$	k/dm^3 mol ⁻¹ s ⁻¹
(i) $\mathbf{R} = p - MeO$	15.3	0.515	1.1	2.2
		1.29	3.0	
		7.73	16	
		19.3	40	
	25.1	See Fig. 1		4.8
	35.0	0.515	5.0	9.8
		1.29	12.5	
		7.73	75	
	47.3	0.515	11	21
		1.29	28	
		7.73	160	
(ii) $\mathbf{R} = \mathbf{H}$	13.7	0.774	1.1	1.5
		7.74	12	
		19.4	29	
	25.2	See Fig. 1		
	36.0	0.414	3.2	7.8
		0.774	6.0	
		7.74	60	
		19.4	150	
	50.0	0.414	8.2	20
		0.774	15	
		7.74	155	
(iii) $\mathbf{R} = o$ -Me	25.0	See Fig. 1		1.6
	34.0	1.55	4.5	3.0
		3.09	9.4	
	48.6	1.55	12	7.9
		3.09	25	

 Table 2
 Rate constants for Tl³⁺ ion promotion^a

(a) Effects of temperature and $[Tl^{3+}]$ ($[H_3O^+] = 0.40 \text{ mol } dm^{-3}$; ionic strength = 0.50 mol dm^{-3})

	<i>T</i> /°C	[Tl ³⁺]/10 ⁻³ mol dm ⁻³	$k_{obs}/10^{-4}$ s ⁻¹	$k/10^{-3}$ dm ³ mol ⁻¹ s ⁻¹
(i) $\mathbf{R} = p$ -MeO	25.0	1.67	0.16	8.2
		3.34	0.30	
		9.81	0.84	
	35.5	See Fig. 2		18
	45.2	1.67	0.82	43
		3.34	1.6	
		6.68	3.0	
(ii) $\mathbf{R} = \mathbf{H}$	25.2	2.95	0.16	3.6
		5.50	0.25	
		9.43	0.40	
	36.7	See Fig	g. 2	11
	43.5	1.69	0.48	23
		5.02	1.25	
		7.88	1.9	
(iii) $\mathbf{R} = p \cdot \mathbf{NO}_2$	25.1	2.95	0.11	1.15
		5.89	0.15	
		10.6	0.20	
	36.7	See Fig	g. 2	5.3
	43.9	2.95	0.69	13
		7.88	1.35	

(b) Effect of $[H_3O^+]$ (R = H; T = 25 °C; $[Tl^{3+}] = 5.54 \times 10^{-3} \text{ mol} dm^{-3}$; ionic strength = 0.99 mol dm⁻³).

[H ₃ O ⁺]/r	nol dm ⁻³ $k_{obs}/10^{-4}$ s ⁻¹
0.28	0.41
0.40	0.40
0.96	0.38

^{*a*} [RC₆H₄NCS]_{initial} = $2-5 \times 10^{-5}$ mol dm⁻³; k_{obs} = observed first-order rate constant; k = average second-order rate constant (see text); ionic strength = 0.50 mol dm⁻³; [H₃O⁺] = 0.050 mol dm⁻³



Fig. 1 Dependence of k_{obs} on [Hg²⁺] at 25.1 \pm 0.1 °C (*a*): *p*-MeO; (*b*): *p*-H; (*c*): *o*-Me

(ii) Thallium(III) Ion Promotion.—The simple kinetic pattern found for Hg^{2+} ion-promotion is also shown by TI^{3+} ions: the promoted hydrolyses are first-order in the isothiocyanate and TI^{3+} ion concentrations, and k_{obs} is largely independent of $[H_3O^+]$ over the range studied (Table 2, Fig. 2). Again a change in R in I from NO₂ to MeO leads to a relatively small, although larger, increase in k (Tables 2 and 3). The acceleratory effect of an increase in ionic strength appears more important in TI^{3+} ion promotion (over the narrow range studied) but the most striking feature is the relative ineffectiveness of TI^{3+} compared with Hg^{2+} ions (Table 3). In a wide variety of soft metal ion promoted reactions of organosulphur compounds Hg^{2+} and

(c) Effect of ionic strength, $I(R = H; T = 25 \text{ °C}; [Tl^{3+}] = 5.54 \times 10^{-3} \text{ mol dm}^{-3}; [H_3O^+] = 0.40 \text{ mol dm}^{-3}$).

$I/mol dm^{-3}$	$k_{\rm obs}/10^{-4} {\rm s}^{-1}$	
0.43	0.23	
0.68	0.30	
0.99	0.40	
0.99	0.40	

^{*a*} [RC₆H₄NCS]_{initial} = $2-5 \times 10^{-5}$ mol dm⁻³; for k_{obs} see Table 1; k = second-order rate constant from the slope of plot of k_{obs} vs. [Tl³⁺].

 Tl^{3+} ions are found to have comparable reactivities as promoters,⁶ whereas in the present system Tl^{3+} ions are *ca*. 5×10^2 to 10^3 fold less effective than are Hg^{2+} ions. Tl^{3+} ions have a similar, or even lower, reactivity than Ag^+ ions in this reaction², a very unusual situation.

There are two other features of the results with Tl³⁺ ions to be noted. (i) Owing to the relative slowness of the promoted reactions, the spontaneous reactions of the isothiocyanates with water are not entirely negligible in these systems, and lead to detectable (but very approximate) intercepts on the k_{obs} axis in plots such as those in Fig. 2. Mostly k_{obs} for the spontaneous reaction is $< 10^{-5}$ s⁻¹; the *p*-NO₂ derivative is the most reactive of the three studied. The intercepts are compatible with the few results available for the spontaneous hydrolyses.^{4,7,8} (ii) Although the pattern of k values for the different isothiocvanates is similar with Hg^{2+} and Tl^{3+} ion promotion, the pattern of activation parameters is very different (Table 3). More dramatic variations are found with Tl^{3+} ions, but the changes in ΔH^{\ddagger} and ΔS^{\ddagger} largely compensate each other. It is noticeable that for the least reactive compound ($R = NO_2$) ΔS^{\ddagger} is positive. These trends, and the low reactivity of Tl^{3+} ions in this reaction, suggest to us that Tl³⁺ ions have relatively great difficulty in coordinating with isothiocyanates. We have previously^{9,10} found evidence that when metal ion-substrate coordination is difficult, more water molecules of solvation tend to be lost from

Table 3 Activation parameters and relative reactivities

$\frac{R \text{ in } RC_6H_4NCS}{R}$	$k^{a}/dm^{3} mol^{-1} s^{-1}$	$\Delta H^{\ddagger}/\text{kJ} \text{ mol}^{-1}$	$\Delta S^{\ddagger}/J \text{ K}^{-1} \text{ mol}^{-1}$
(i) Hg ²⁺ ion prof	motion		
$p-NO_2^b$	1.45	56 ± 2	-53 + 4
Ĥ	3.8	52 ± 2	-58 ± 2
p-MeO	4.8	52 ± 2	-56 ± 2
o-Me	1.6	52 ± 2	-67 ± 2
(ii) Tl ³⁺ ion prom	notion		
$p-NO_2$	1.15×10^{-3}	99 ± 6	30 ± 10
Ĥ	3.6×10^{-3}	78 ± 3	-30 ± 4
p-MeO	8.2×10^{-3}	63 ± 5	-74 ± 8

^{*a*} Second-order rate constant at 25.1 \pm 0.1 °C. ^{*b*} Ref. 2.

the metal ion when forming the adduct with the substrate. This can lead to large positive values of ΔS for adduct formation, and ΔH tends to be less negative. We suggest such an effect could underlie the trend in the activation parameters for the Tl³⁺ ion reactions. If we assume a mechanism for Tl³⁺ ion promotion [eqns. (5)–(7)], analogous to that suggested for Hg²⁺ ions, then $k_{obs} = k_{T1} K_{T1} [Tl^{3+}]$. The observed activation parameters will contain a contribution from both steps (5) and (6). An especially large positive ΔS value for step (5) with the *p*-NO₂ derivative may account for the overall positive ΔS^{t} value in this case, even if ΔS^{t} for step (6) is negative. Another feature of the results that suggests the relatively low reactivity of Tl³⁺ ions in these hydrolyses arises from their difficulty in forming adducts III with isothiocyanates, is the larger effect of ionic strength on k_{obs} than with Hg²⁺ or Ag⁺ ion promotion: we have always found that



Fig. 2 Dependence of k_{obs} on $[Tl^{3+}]$ (*a*): *p*-OMe (35.5 °C); (*b*): *p*-H (36.7 °C); (*c*): *p*-NO₂ (36.7 °C)

increases in the ionic strength accelerate soft metal ion promoted reactions when the pre-equilibria lie well to the left.⁶ Our comparisons of Hg^{2+} and Tl^{3+} ion promotion in other contexts⁶ suggests that for Tl^{3+} ions to exhibit a reactivity comparable to that of Hg^{2+} ions a chelating substrate may be required.

$$RC_{6}H_{4}NCS + Tl^{3+} \xrightarrow{\text{max}} RC_{6}H_{4}NCS \longrightarrow Tl^{3+} \quad K_{Tl}$$
(5)

$$III + 2 H_2O \xrightarrow{\text{slow}} RC_6H_4N = C -S -Tl^{2+} + H_3O \qquad k_{Tl} \qquad (6)$$

$$RC_{6}H_{4}NH_{2} + [TIS^{+}] + CO_{2} + 2H_{3}O^{+} \xleftarrow{fast}{H_{2}O} RC_{6}H_{4}NHC - S - TI^{2+} + H_{3}O^{+}$$
(7)

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