

Table 1 Rate constants for Hg²⁺ ion promotion^a

	<i>T</i> /°C	[Hg ²⁺]/10 ⁻³ mol dm ³	<i>k</i> _{obs} /10 ⁻³ s ⁻¹	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹		
(i) R = <i>p</i> -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		
	0.515		11	21		
	47.3	1.29	28			
		7.73	160			
		(ii) R = H	13.7		0.774	1.1
7.74				12		
19.4	29					
See Fig. 1						
25.2	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) R = <i>o</i> -Me		25.0		See Fig. 1	
34.0		4.5		3.0		
48.6		3.09	9.4	7.9		
		1.55	12			
		3.09	25			
		1.55	12			

^a [RC₆H₄NCS]_{initial} = 2–5 × 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

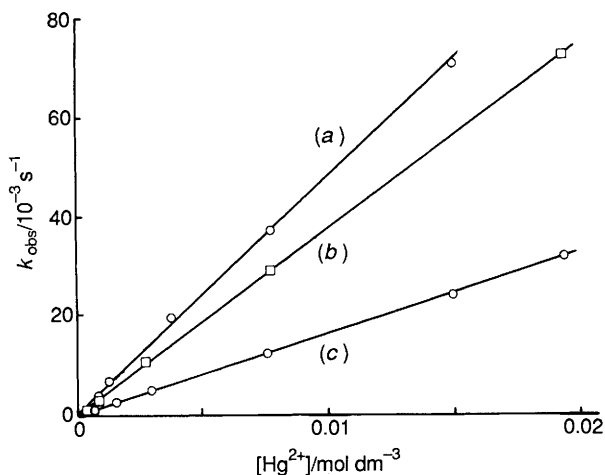


Fig. 1 Dependence of *k*_{obs} on [Hg²⁺] at 25.1 ± 0.1 °C (a): *p*-MeO; (b): *p*-H; (c): *o*-Me

(ii) *Thallium(III) Ion Promotion*.—The simple kinetic pattern found for Hg²⁺ ion-promotion is also shown by Tl³⁺ ions: the promoted hydrolyses are first-order in the isothiocyanate and Tl³⁺ ion concentrations, and *k*_{obs} is largely independent of [H₃O⁺] 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 Tl³⁺ ion promotion (over the narrow range studied) but the most striking feature is the relative ineffectiveness of Tl³⁺ compared with Hg²⁺ ions (Table 3). In a wide variety of soft metal ion promoted reactions of organosulphur compounds Hg²⁺ and

Table 2 Rate constants for Tl³⁺ ion promotion^a

(a) Effects of temperature and [Tl ³⁺] ([H ₃ O ⁺] = 0.40 mol dm ⁻³ ; ionic strength = 0.50 mol dm ⁻³)						
	<i>T</i> /°C	[Tl ³⁺]/10 ⁻³ mol dm ³	<i>k</i> _{obs} /10 ⁻⁴ s ⁻¹	<i>k</i> /10 ⁻³ dm ³ mol ⁻¹ s ⁻¹		
(i) R = <i>p</i> -MeO	25.0	1.67	0.16	8.2		
		3.34	0.30			
		9.81	0.84			
		See Fig. 2				
	35.5	See Fig. 2			18	
		45.2	1.67	0.82		43
			3.34	1.6		
			6.68	3.0		
See Fig. 2						
(ii) R = H	25.2	2.95	0.16	3.6		
		5.50	0.25			
		9.43	0.40			
		See Fig. 2				
	36.7	See Fig. 2			11	
		43.5	1.69	0.48		23
			5.02	1.25		
			7.88	1.9		
See Fig. 2						
(iii) R = <i>p</i> -NO ₂	25.1	2.95	0.11	1.15		
		5.89	0.15			
		10.6	0.20			
		See Fig. 2				
	36.7	See Fig. 2			5.3	
		43.9	2.95	0.69		13
			7.88	1.35		
			See Fig. 2			

(b) Effect of [H₃O⁺] (R = H; *T* = 25 °C; [Tl³⁺] = 5.54 × 10⁻³ mol dm⁻³; ionic strength = 0.99 mol dm⁻³).

[H ₃ O ⁺]/mol dm ⁻³	<i>k</i> _{obs} /10 ⁻⁴ s ⁻¹
0.28	0.41
0.40	0.40
0.96	0.38

(c) Effect of ionic strength, *I* (R = H; *T* = 25 °C; [Tl³⁺] = 5.54 × 10⁻³ mol dm⁻³; [H₃O⁺] = 0.40 mol dm⁻³).

<i>I</i> /mol dm ⁻³	<i>k</i> _{obs} /10 ⁻⁴ s ⁻¹
0.43	0.23
0.68	0.30
0.99	0.40

^a [RC₆H₄NCS]_{initial} = 2–5 × 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⁺].

Tl³⁺ ions are found to have comparable reactivities as promoters,⁶ whereas in the present system Tl³⁺ ions are *ca.* 5 × 10² to 10³ fold less effective than are Hg²⁺ ions. Tl³⁺ ions have a similar, or even lower, reactivity than Ag⁺ ions in this reaction², a very unusual situation.

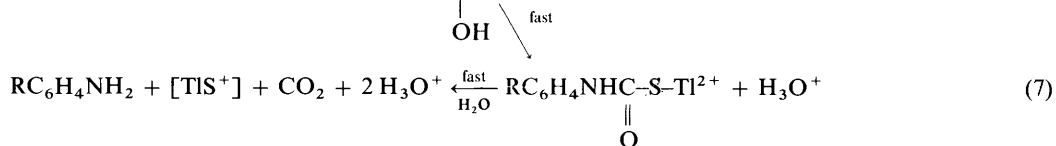
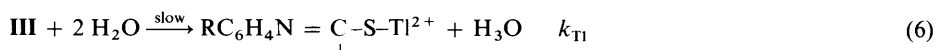
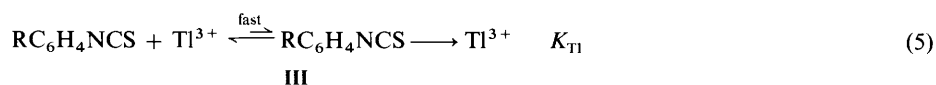
There are two other features of the results with Tl³⁺ ions to be noted. (i) Owing to the relative slowness of the promoted reactions, the spontaneous reactions of the isothiocyanates with water are not entirely negligible in these systems, and lead to detectable (but very approximate) intercepts on the *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 isothiocyanates is similar with Hg²⁺ and Tl³⁺ ion promotion, the pattern of activation parameters is very different (Table 3). More dramatic variations are found with Tl³⁺ ions, but the changes in Δ*H*[‡] and Δ*S*[‡] largely compensate each other. It is noticeable that for the least reactive compound (R = NO₂) Δ*S*[‡] is positive. These trends, and the low reactivity of Tl³⁺ 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

R in RC ₆ H ₄ NCS	<i>k</i> ^a /dm ³ mol ⁻¹ s ⁻¹	Δ <i>H</i> [‡] /kJ mol ⁻¹	Δ <i>S</i> [‡] /J K ⁻¹ mol ⁻¹
(i) Hg ²⁺ ion promotion			
<i>p</i> -NO ₂ ^b	1.45	56 ± 2	-53 ± 4
H	3.8	52 ± 2	-58 ± 2
<i>p</i> -MeO	4.8	52 ± 2	-56 ± 2
<i>o</i> -Me	1.6	52 ± 2	-67 ± 2
(ii) Tl ³⁺ ion promotion			
<i>p</i> -NO ₂	1.15 × 10 ⁻³	99 ± 6	30 ± 10
H	3.6 × 10 ⁻³	78 ± 3	-30 ± 4
<i>p</i> -MeO	8.2 × 10 ⁻³	63 ± 5	-74 ± 8

^a Second-order rate constant at 25.1 ± 0.1 °C. ^b Ref. 2.

the metal ion when forming the adduct with the substrate. This can lead to large positive values of Δ*S* for adduct formation, and Δ*H* 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 $k_{\text{obs}} = k_{\text{Tl}} K_{\text{Tl}} [\text{Tl}^{3+}]$. The observed activation parameters will contain a contribution from both steps (5) and (6). An especially large positive Δ*S* value for step (5) with the *p*-NO₂ derivative may account for the overall positive Δ*S*[‡] value in this case, even if Δ*S*[‡] 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



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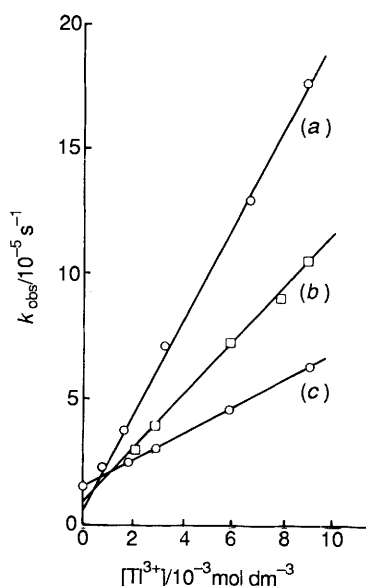


Fig. 2 Dependence of *k*_{obs} on [Tl³⁺]: (a): *p*-OMe (35.5 °C); (b): *p*-H (36.7 °C); (c): *p*-NO₂ (36.7 °C)

increases in the ionic strength accelerate soft metal ion promoted reactions when the pre-equilibria lie well to the left.⁶ Our comparisons of Hg²⁺ and Tl³⁺ ion promotion in other contexts⁶ suggests that for Tl³⁺ ions to exhibit a reactivity comparable to that of Hg²⁺ ions a chelating substrate may be required.

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