The Kinetics and Mechanism of the Thallium Ion-promoted Hydrolysis of Thiol Esters

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The kinetics of the thallium(III) ion-promoted hydrolysis of three *para*-substituted *S*-ethyl thiobenzoates have been studied. The hydrogen ion-catalysed reaction is very slow by comparison. The sequence of ester reactivity in the promoted hydrolysis is p-MeO $>$ p-H $\gg$ p-NO_2. The substituent effects, the values of the activation parameters and the effects of changes in ionic strength all suggest that the hydrolysis mechanism is $A_{Ac}2$ for the p-NO_2 derivative, but $A_{Ac}1$ for the other esters. In the $A_{Ac}2$ mechanism the rate acceleration produced by Tl^{3+} ions is comparable with that produced by Ag^+ ions and much smaller than those produced by Hg^{2+} or by Hg_2^{2+} ions. However, in the $A_{Ac}1$ route the effect of Tl^{3+} is greater and comparable with that of Hg_2^{2+}. These effects suggest the $A_{Ac}2$ route is intramolecular.

KINETIC studies of the soft metal ion-promoted hydrolysis of thiol esters [reaction (1)] have shown [1,2] that Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} ions have little or no effect on the

$$RC_6H_4COSEt + M^{n+} + 2H_2O \longrightarrow RC_6H_4CO_2H + EtSM^{(n-1)+} + H_3O^+ \quad (1)$$

rate, whereas Hg^{2+}, Hg_2^{2+}, and Ag^+ ions have powerful effects. For substituted *S*-ethyl thiobenzoates (p-H, p-NO_2, and p-MeO) in a dilute (*ca.* 10^{-2} mol dm^{-3}) solution of hydrogen ions previous results suggest that the rate-determining step in the silver ion-promoted reactions is bimolecular for all three esters, while in the mercury(II) and mercury(I) ion-promoted reactions there is a transition from a bimolecular rate-determining step for the p-nitro ester to a unimolecular rate-determining step for the p-methoxy ester. Catalysis by hydrogen ions contributes negligibly in the presence of Ag^+, Hg_2^{2+}, or Hg^{2+} ions, whose strengths as promoters are in the sequence $Hg^{2+} > Hg_2^{2+} > Ag^+$.

Another potentially powerful soft acid [3] which has received little attention as a catalyst is Tl^{3+}. It is known to promote the hydrolysis of thioacetals [4] and of thioamides.[5] Its reactivity in the hydrolysis of thioamides is comparable with that of Hg^{2+}, but it is less effective [6] than Hg^{2+} and Hg_2^{2+} in displacing other metal ions from RCH_2M^{n+}. We now report a kinetic study of the thallium(III) ion-promoted hydrolysis of thiol esters and compare the results with those for the mercury(II), mercury(I), and silver ions.

EXPERIMENTAL

Materials.—All solutions were made up with freshly distilled water. AnalaR ethanol, aqueous perchloric acid (70%), and thallium(III) nitrate were used without further purification. The perchloric acid was standardised with potassium iodate. AnalaR sodium perchlorate was dried at 150 °C before use.

S-Ethyl thiobenzoate, *S*-ethyl p-nitrothiobenzoate, and *S*-ethyl p-methoxythiobenzoate were previous samples.[2]

Reaction Mixtures.—Stock solutions of the esters were made up by weight in ethanol. Ethanol was used to facilitate the dissolution of the ester in the final aqueous reaction mixture which contained 2% (v/v) ethanol. Stock solutions of thallium nitrate were made up by weight in aqueous perchloric acid. The flasks containing the stock thallium nitrate solutions and the final mixtures were wrapped in aluminium foil to exclude light. Mixtures were made up by volume and contained at least 0.4 mol dm^{-3} perchloric acid to prevent the precipitation of thallium as hydroxide. Mixtures normally also contained sufficient sodium perchlorate to give a total ionic strength of 0.5 mol dm^{-3}.

Kinetic Arrangements.—Reactions were followed by observing the changes in the u.v. spectrum in the region 290—320 nm using a Unicam SP 500 spectrophotometer which (for the faster reactions) was fitted with an external Servoscribe chart recorder.

For most reactions the thallium ion was present in at least a 10-fold excess over the ester ([ester] 1×10^{-4} mol dm^{-3}). Under these conditions the reactions showed good first-order behaviour over at least three half-lives. Preliminary values of the first-order rate constant ($k_{obs.}$) were obtained from plots of ln ($A - A_\infty$) against time, where A and A_∞ were the absorbance readings at the chosen wavelength at time t and at infinite time, respectively. A_∞ was determined after at least 10 half-lives. Refined values of $k_{obs.}$ were obtained with the aid of a computer program [7] that involved an extension of the method of linear least-squares. Values of $k_{obs.}$ calculated in this way were normally reproducible to within ±5%. However, for those runs in which the thallium ion was present in less than a 10-fold excess of the ester (*i.e.* [Tl^{3+}] $\leqslant 1 \times 10^{-3}$ mol dm^{-3}) the first-order plots deviated from linearity. In these circumstances $k_{obs.}$ was obtained from the initial slopes and values were reproducible to within ±10%. For all the systems studied the contribution to the rate of hydrolysis from hydrogen ion or from solvent catalysis was negligible.

Products.—For each ester preparative-scale experiments were carried out using concentration conditions ([ester] 5×10^{-3} mol dm^{-3}, [Tl^{3+}] 1×10^{-2} mol dm^{-3}, [H_3O^+] 0.4 mol dm^{-3}, solvent 10% v/v ethanol–water) as close as feasible to those of the kinetic runs. In each case the expected benzoic acid was obtained in >85% yield. The u.v. spectral changes observed in the kinetic runs also indicated that the products were formed in very high (*ca.* 100%) yield. The mercaptide products (and their decomposition products) were obtained as a dark brown precipitate from the preparative-scale experiments. The departure from first-order behaviour when [Tl^{3+}] $< 1 \times 10^{-3}$ mol dm^{-3} is evidence for the removal of the thallium ion by the ethanethiol product. Since thallium(III) derivatives of thiols are relatively unstable,[8] it is assumed that $EtSTl^{2+}$-$(ClO_4^-)_2$ was initially formed, and subsequently decomposed to a thallium(I) derivative.

RESULTS AND DISCUSSION

Kinetics of Hydrolysis.—Values of $k_{\text{obs.}}$ are given in Table 1. For each ester, at fixed pH and temperature, plots of $k_{\text{obs.}}$ against [Tl^{3+}] are rectilinear and pass through the origin. This was also demonstrated by computing, for each set of $k_{\text{obs.}}$ values, a linear least squares fit to the equation $k_{\text{obs.}} = a + k_1[Tl^{3+}]$. In all cases the constant *a* was comparatively very small, was sometimes positive and sometimes negative, and had an error which sometimes overlapped the origin. We conclude that, within the limits of our experimental error, $k_{\text{obs.}} = k_1[Tl^{3+}]$. The computed values of the second-order rate constants, k_1, are in Table 2.

TABLE 1

Selected values of $k_{\text{obs.}}$ for the thallium ion-promoted hydrolysis of thiol esters showing dependence on [Tl^{3+}]. [Ester] *ca.* 1×10^{-4} mol dm^{-3}, [H_3O^+] 0.4 mol dm^{-3}, ionic strength 0.5 mol dm^{-3}, solvent 2% v/v ethanol–water, [Tl^{3+}] in mol dm^{-3}, $k_{\text{obs.}}$ in s^{-1}

S-Ethyl *p*-nitrothiobenzoate at 60.31 ± 0.20 °C								
10^3 [Tl^{3+}]	1.64	2.48	3.30	4.13	4.96			
10^6 $k_{\text{obs.}}$	1.15	1.85	2.71	3.33	3.76			
S-Ethyl thiobenzoate at 25.42 ± 0.05 °C								
10^3 [Tl^{3+}]	1.71	3.42	5.13	6.84	8.55	10.3	12.0	
10^5 $k_{\text{obs.}}$	0.709	1.30	2.08	2.69	3.14	3.82	4.50	
S-Ethyl *p*-methoxythiobenzoate at 25.80 ± 0.05 °C								
10^3 [Tl^{3+}]	0.794	1.59	2.38	3.18	3.97	5.96	7.94	8.14
10^3 $k_{\text{obs.}}$	0.299	0.599	0.916	1.24	1.52	2.28	3.11	3.20

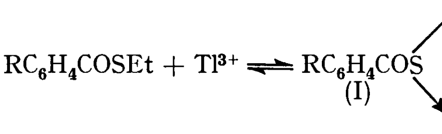
TABLE 2

Values of k_1 and of the activation parameters. Units of k_1 are mol^{-1} dm^3 s^{-1}, of $\Delta H^{\ddagger}$ kcal mol^{-1} (kJ mol^{-1}), and of $\Delta S^{\ddagger}$ cal mol^{-1} K^{-1} (J mol^{-1} K^{-1})

t/°C	10^2 k_1	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
S-Ethyl *p*-nitrothiobenzoate			
60.31	0.0841 ± 0.0041		
S-Ethyl thiobenzoate			
25.42	0.370 ± 0.008		
35.48	1.05 ± 0.02		
45.28	3.47 ± 0.07	21.8 ± 0.4	3.3 ± 1.2
58.20	15.0 ± 0.4	(91 ± 2)	(14 ± 5)
S-Ethyl *p*-methoxythiobenzoate			
25.80	39.1 ± 0.2		
35.40	102 ± 3		
45.05	252 ± 2	16.7 ± 0.3	−4.6 ± 0.9
59.70	787 ± 27	(70 ± 1)	(−19 ± 4)

The *p*-nitro ester was only studied at 60.31 °C. At this temperature the reaction was so slow that lowering the temperature was hardly practicable. Our attempts to use significantly higher temperatures were unsuccessful as the values of $k_{\text{obs.}}$ then became very irreproducible. The k_1 values for the other two esters at the various temperatures (Table 2) were used to calculate the enthalpies and entropies of activation by computing the linear least squares fit to the equation $\ln(k_1/T) = \ln(k/T) - \Delta H^{\ddagger}/(RT) + \Delta S^{\ddagger}/R$. These computed values are also in Table 2.

As with both the mercury(II) ion and the mercury(I) ion promotion, the sequence of reactivity (Table 2) of the esters towards the thallium ion is *p*-MeO > *p*-H > *p*-NO$_2$, this being the opposite to that found for the silver ion.[1,2] However, although the ratio of reactivities of the *p*-H and *p*-MeO esters (*ca.* 100) is very similar to that shown in the presence of Hg^{2+} and Hg_2^{2+}, the ratio of the reactivity of the *p*-H to that of the *p*-NO$_2$ ester (*ca.* 500) is very much greater than that shown in the presence of either Hg^{2+} or Hg_2^{2+} (*ca.* 10—20). Furthermore, the lower $\Delta H^{\ddagger}$ value (Table 2) for the *p*-MeO ester compared with that for the *p*-H ester is in line with the trend found for the mercury(II) and the mercury(I) ions and is opposite to that found for the silver ion. It is also noteworthy that the $\Delta S^{\ddagger}$ values (Table 2) for these two esters are also numerically small, as they are in promotion by the mercury ions, and not significantly negative as they are in silver ion promotion. Taken together these facts clearly suggest that, for the *p*-H and *p*-MeO esters the mechanisms underlying the thallium ion promotion are similar to those underlying promotion by mercury ions and different from those underlying the silver ion promotion. We therefore suggest an $A_{\text{Ac}}1$ mechanism [equations (2)—(4)] for the *p*-MeO and *p*-H esters with thallium(III).



$$RC_6H_4COSEt + Tl^{3+} \rightleftharpoons RC_6H_4CO\overset{Et}{\underset{Tl^{3+}}{S}} \quad \text{(I)} \qquad \text{Fast} \quad (2)$$

$$\text{(I)} \longrightarrow RC_6H_4CO^+ + EtSTl^{2+} \qquad \text{Slow} \quad (3)$$

$$RC_6H_4CO^+ + 2H_2O \longrightarrow RC_6H_4CO_2H + H_3O^+ \qquad \text{Fast} \quad (4)$$

The activation parameters for the mercury(II) and the mercury(I) ion promotion of the *p*-NO$_2$ ester hydrolysis, and for the silver ion promotion of hydrolysis of all three esters, suggest an $A_{\text{Ac}}2$ mechanism for these systems.[1,2] Although the activation parameters could not be obtained for the thallium ion-promoted hydrolysis of the *p*-NO$_2$ ester, it is noteworthy that if a $\rho\sigma$ relation is assumed for the *p*-MeO and *p*-H esters, then the value predicted for k_1 for the *p*-NO$_2$ ester is *ca.* 300-fold smaller than the experimental value. Since a similar result is obtained using the data for the Hg^{2+} and the Hg_2^{2+} ions it seems probable that for the thallium ion reaction, as for those promoted by mercury ions, a change to an $A_{\text{Ac}}2$ route [equations (5) and (6)] occurs for the *p*-NO$_2$ ester.

$$\text{(I)} + H_2O \longrightarrow RC_6H_4CO_2H_2^+ + EtSTl^{2+} \qquad \text{Slow} \quad (5)$$

$$RC_6H_4CO_2H_2^+ + H_2O \longrightarrow RC_6H_4CO_2H + H_3O^+ \qquad \text{Fast} \quad (6)$$

Effect of pH.—The effect of pH changes on the value of $k_{\text{obs.}}$ for the *p*-MeO ester is shown in Table 3. It is known that the thallium ion is hydrated and that the coordinated water undergoes acid dissociation[9] as in

TABLE 3

Effect of $[H_3O^+]$ on $k_{obs.}$ for the thallium ion promoted hydrolysis of *S*-ethyl *p*-methoxythiobenzoate. [Ester] *ca.* 1×10^{-4} mol dm^{-3}, ionic strength 1.0 mol dm^{-3}, solvent 2% v/v ethanol–water, *t* 25.80 ± 0.05 °C, $[H_3O^+]$ in mol dm^{-3}, $k_{obs.}$ in s^{-1}

$[Tl^{3+}]$ 2.22×10^{-3} mol dm^{-3}

$[H_3O^+]$	0.190	0.405	0.666
$10^3\ k_{obs.}$	1.38	1.50	1.54

$[Tl^{3+}]$ 8.32×10^{-3} mol dm^{-3}

$[H_3O^+]$	0.405	0.506	0.749	0.910
$10^3\ k_{obs.}$	5.63	5.77	5.76	5.76

equations (7) and (8). Over the pH range studied by us the predominant species is (II). At $[H_3O^+]$ 0.9 mol dm^{-3}

$$\underset{\text{(II)}}{[\mathrm{Tl(H_2O)}_n]^{3+}} + \mathrm{H_2O} \overset{K_1}{\rightleftharpoons} \underset{\text{(III)}}{[\mathrm{Tl(H_2O)}_{n-1}\mathrm{OH}]^{2+}} + \mathrm{H_3O^+} \quad (7)$$

$$K_1\ 0.07\ \text{mol dm}^{-3}\ \text{at}\ 25\ °\text{C}$$

$$\text{(III)} + \mathrm{H_2O} \overset{K_2}{\rightleftharpoons} \underset{\text{(IV)}}{[\mathrm{Tl(H_2O)}_{n-2}(\mathrm{OH})_2]^{+}} + \mathrm{H_3O^+} \quad (8)$$

$$K_2\ 0.03\ \text{mol dm}^{-3}\ \text{at}\ 25\ °\text{C}$$

ca. 93% of the thallium ion will exist as (II); this percentage falls to *ca.* 84% for $[H_3O^+]$ 0.4 mol dm^{-3} and to *ca.* 70% at $[H_3O^+]$ 0.2 mol dm^{-3}. The concentrations of species (III) and (IV) change (increase) by much larger factors (by *ca.* 4- and 16-fold, respectively) over the same hydrogen ion concentration range. The results in Table 3 therefore strongly suggest that species (III) and (IV) cannot be providing most of the catalysis and that species (II) makes the major contribution to the catalysis in this region. This is a sensible result compatible with the higher concentration of (II) and with its greater charge.

Effect of Ionic Strength.—Whereas an increase in ionic strength from 0.5 to 1.0 mol dm^{-3} has very little effect on $k_{obs.}$ for the *p*-NO_2 ester, the same increase leads to a marked rise in the $k_{obs.}$ values for both the *p*-H and the *p*-MeO esters (see Table 4). For the latter esters plots of log $k_{obs.}$ *versus* $I^{\frac{1}{2}}$ are straight lines. These effects are in keeping with the proposed mechanisms, since the separation of charge will be greater in the transition state for the $A_{Ac}1$ process than for the $A_{Ac}2$ process.

TABLE 4

Effect of ionic strength on $k_{obs.}$ for the thallium ion-promoted hydrolysis of thioesters. [Ester] *ca.* 1×10^{-4} mol dm^{-3}, $[H_3O^+]$ 0.4 mol dm^{-3}, solvent 2% v/v ethanol–water, ionic strength *I* in mol dm^{-3}, $k_{obs.}$ in s^{-1}

S-Ethyl *p*-nitrothiobenzoate at 60.31 ± 0.20 °C, $[Tl^{3+}]$ 4.99×10^{-3} mol dm^{-3}

I	0.5	0.75	1.0
$10^6\ k_{obs.}$	3.76	3.76	3.99

S-Ethyl thiobenzoate at 25.42 ± 0.05 °C, $[Tl^{3+}]$ 1.21×10^{-2} mol dm^{-3}

I	0.5	0.75	1.0
$10^5\ k_{obs.}$	4.50	5.40	6.40

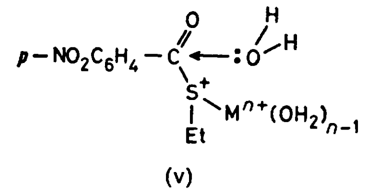
S-Ethyl *p*-methoxythiobenzoate at 25.80 ± 0.05 °C, $[Tl^{3+}]$ 8.32×10^{-4} mol dm^{-3}

I	0.05	0.75	1.0
$10^4\ k_{obs.}$	3.23	4.26	4.57

$[Tl^{3+}]$ 8.32×10^{-3} mol dm^{-3}

I	0.5	0.75	1.0
$10^3\ k_{obs.}$	3.21	4.39	5.63

Comparison of the Efficiencies of Tl^{3+}, Hg_2^{2+}, Hg^{2+}, *and* Ag^+ *as Promoters.*—The relative catalytic effectiveness of the metal ions depends on the type of mechanism followed. For the $A_{Ac}1$ route their efficiencies lie in the sequence $Hg^{2+} > Tl^{3+} \simeq Hg_2^{2+} \gg Ag^+$ and for the $A_{Ac}2$ route in the sequence $Hg^{2+} > Hg_2^{2+} \gg Tl^{3+} \gg Ag^+$. The position of thallium in the former sequence probably reflects the ability of the triply charged thallium to withdraw electrons from the C–S bond and thus aid acylium ion formation. Its much lower position in the second sequence means that the high charge on species (I) does not encourage the bimolecular attack of water in reaction (5). We have argued previously that intramolecular routes involving hydroxy species of both the mercury(I) ion and the mercury(II) ion may be important.[2] They are probably important too for the silver ion.[10] The hydrated thallium ion undergoes deprotonation more readily than do the hydrated mercury or silver ions. Thus the thallium ion attracts electrons from the O–H bonds of the attached water molecules more strongly. In an intramolecular route (V), involving a hydrated ion,



(V)

opposing effects will operate. Although the charge on the ion will increase the positive charge on the carbonyl carbon atom, it will at the same time discourage the transfer of OH to the carbon atom by strongly attracting to itself the OH electrons. It is reasonable therefore for such a mechanism to find Tl^{3+} in an intermediate position between Ag^+ and Hg^{2+} as regards efficiency. We are therefore once more led to the conclusion that intramolecular routes are important in the reactions with bimolecular rate-determining steps.

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