# 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 $\mathrm{Hg}^{2+}$ ion-promoted hydrolysis of $\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}$ a large increase in electron-release by R produces only a small increase in reaction rate. These substituent effects support the mechanism previously proposed. $\mathrm{Tl}^{3+}$ ions are surprisingly much (ca. $10^{3}$-fold) less effective in promoting the hydrolyses than are $\mathrm{Hg}^{2+}$ ions, but show the same kinetic form and similar substituent effects. A similar mechanism is suggested. The low reactivity of $\mathrm{Tl}^{3+}$ ions, the different pattern of their activation parameters, and the greater dependence of the $\mathrm{Tl}^{3+}$ ion-promotion on ionic strength, all suggest that these ions form adducts with isothiocyanates with special difficulty; the comparable reactivity normally found for $\mathrm{Hg}^{2+}$ and $\mathrm{Tl}^{3+}$ 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

$$
\begin{align*}
\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}+\mathrm{H}_{2} \mathrm{O} & {\left[\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NHCOSH}\right] }
\end{align*} \mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NH}_{2}+[\mathrm{COS}]\left(\xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{H}_{2} \mathrm{~S}+\mathrm{CO}_{2}\right) .
$$

significantly catalysed only at relatively high ( $>8.0 \mathrm{~mol} \mathrm{dm}^{-3}$ ) concentrations of hydrogen ions and (ii) that low concentrations of $\mathrm{Ag}^{+}$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 $\mathrm{Tl}^{3+}$ ion-promoted hydrolysis, and on the effects of substituents in the isothiocyanate on the rates of the $\mathrm{Hg}^{2+}$ and $\mathrm{Tl}^{3+}$ ion-promoted reactions.

## Experimental

The materials were mostly previous samples. ${ }^{1,2}$ Thallium(iII) nitrate was of AnalaR grade. In the $\mathrm{Hg}^{\mathbf{2 +}}$ ion-promotion the kinetics were studied essentially as before, ${ }^{2}$ and the loss of isothiocyanate absorption was monitored at the absorption maximum. With $\mathrm{Tl}^{3+}$ ions it was necessary to maintain $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>0.2 \mathrm{~mol} \mathrm{dm}{ }^{-3}$ to avoid precipitation of the metal hydroxide during these relatively slow runs. ${ }^{3}$ Otherwise the conditions were similar to those used with $\mathrm{Hg}^{2+}$ 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, $k_{\text {obs }}$, were reproducible to within $\pm 6 \%$ with $\mathrm{Hg}^{2+}$ ions, and to within $\pm 12 \%$ with $\mathrm{Tl}^{3+}$ 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 $\mathrm{Hg}^{2+}$ ion promotion, and contributed little to the observed rates in the $\mathrm{Tl}^{3+}$ ion systems.

## Results and Discussion

(i) Mercury(iII) Ion Promotion.--Our previous work ${ }^{2}$ with $p$-nitrophenyl isothiocyanate showed the reaction to be firstorder in the isothiocyanate and $\mathrm{Hg}^{2+}$ ion concentrations, and to have $\Delta S^{\ddagger}=-58 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$. Changes in $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$(up to 0.3 $\mathrm{mol} \mathrm{dm}{ }^{-3}$ ) had no effect on $k_{\mathrm{obs}}$, and an increase in ionic strength led to a modest increase in $k_{\text {obs }}$. We proposed the mechanism given in eqns. (2)-(4) for which $k_{\text {obs }}=k_{\mathrm{Hg}_{8}} K_{\mathrm{Hg}}\left[\mathrm{Hg}^{2+}\right]=$ $k\left[\mathrm{Hg}^{2+}\right]$ where $k$ is the second-order constant. In the present work the hydrolysis of all the isothiocyanates used with $\mathrm{Hg}^{2+}$ ions (Table 1) also display a simple first-order dependence on $\left[\mathrm{Hg}^{2+}\right]$ (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 $K_{\mathrm{Hg}}$ but will probably decrease $k_{\mathrm{Hg}}$. Our results (Tables 1 and 3 ) are in agreement with this prediction, and the small increase in $k$ suggests that the effect on $K_{\mathrm{Hg}}$ is just dominant. (For the simple bimolecular reaction of glycine or $\mathrm{OH}^{-}$ions with phenyl isothiocyanates ${ }^{4}$ a change from the $p-\mathrm{NO}_{2}$ to the $p-\mathrm{MeO}$ 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 $\Delta S^{\ddagger}$ 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 $\mathrm{Hg}^{2+}$ ion-promotion are supportive of the mechanism previously proposed. ${ }^{2}$

$$
\begin{gather*}
\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}+\mathrm{Hg}^{2+} \stackrel{\text { fast }}{\rightleftharpoons} \mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS} \longrightarrow \mathrm{Hg}^{2+} \quad K_{\mathrm{Hg}}  \tag{2}\\
\text { II }+2 \mathrm{H}_{2} \mathrm{O} \xrightarrow{\text { slow }} \mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{~N}=\underset{\mathrm{OH}}{\mathrm{C}-\mathrm{S}-\mathrm{Hg}^{+}}+\mathrm{H}_{3} \mathrm{O}^{+} \quad k_{\mathrm{Hg}}  \tag{3}\\
\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NH}_{2}+\mathrm{HgS}+\mathrm{CO}_{2}+2 \mathrm{H}_{3} \mathrm{O}^{+} \underset{\mathrm{H}_{2} \mathrm{O}}{\text { fast }} \mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NHC}-\mathrm{SH}_{4}-\mathrm{Hg}^{+}+\mathrm{H}_{3} \mathrm{O}^{+}  \tag{4}\\
\|
\end{gather*}
$$

Table 1 Rate constants for $\mathrm{Hg}^{2+}$ ion promotion ${ }^{\text {a }}$

|  | $T /{ }^{\circ} \mathrm{C}$ | $\begin{aligned} & {\left[\mathrm{Hg}^{2+}\right] / 10^{-3}} \\ & \mathrm{~mol} \mathrm{dm}^{3} \end{aligned}$ | $\underset{\mathrm{s}^{-1}}{k_{\text {obs }} / 1 \sigma^{-3}}$ | $\begin{aligned} & k / \mathrm{dm}^{3} \\ & \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| (i) $\mathrm{R}=p-\mathrm{MeO}$ | 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) $\mathrm{R}=\mathrm{H}$ | 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) $\mathrm{R}=o-\mathrm{Me}$ | 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 |  |

${ }^{a}\left[\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}\right]_{\text {initial }}=2-5 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3} ; k_{\text {obs }}=$ observed firstorder rate constant; $k=$ average second-order rate constant (see text); ionic strength $=0.50 \mathrm{~mol} \mathrm{dm}^{-3} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.050 \mathrm{~mol} \mathrm{dm}^{-3}$


Fig. 1 Dependence of $k_{\text {obs }}$ on $\left[\mathrm{Hg}^{2+}\right]$ at $25.1 \pm 0.1^{\circ} \mathrm{C}(a): p-\mathrm{MeO} ;(b)$ : $p-\mathrm{H} ;(c): o-\mathrm{Me}$
(ii) Thallium(iII) Ion Promotion.-The simple kinetic pattern found for $\mathrm{Hg}^{2+}$ ion-promotion is also shown by $\mathrm{Tl}^{3+}$ ions: the promoted hydrolyses are first-order in the isothiocyanate and $\mathrm{Tl}^{3+}$ ion concentrations, and $k_{\mathrm{obs}}$ is largely independent of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$over the range studied (Table 2, Fig. 2). Again a change in R in I from $\mathrm{NO}_{2}$ 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 $\mathrm{Tl}^{3+}$ ion promotion (over the narrow range studied) but the most striking feature is the relative ineffectiveness of $\mathrm{Tl}^{3+}$ compared with $\mathrm{Hg}^{2+}$ ions (Table 3 ). In a wide variety of soft metal ion promoted reactions of organosulphur compounds $\mathrm{Hg}^{2+}$ and

Table 2 Rate constants for $\mathrm{Tl}^{3+}$ ion promotion ${ }^{a}$
(a) Effects of temperature and $\left[\mathrm{Tl}^{3+}\right]\left(\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.40 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right.$; ionic strength $=0.50 \mathrm{~mol} \mathrm{dm}^{-3}$ )

|  | $T /{ }^{\circ} \mathrm{C}$ | $\begin{aligned} & {\left[\mathrm{Tl}^{3+}\right] / 10^{-3}} \\ & \mathrm{~mol} \mathrm{dm}^{-3} \end{aligned}$ | $\begin{aligned} & k_{\text {obs }} / 10^{-4} \\ & \mathrm{~s}^{-1} \end{aligned}$ | $\begin{aligned} & k / 10^{-3} \\ & \mathrm{dm}^{3} \mathrm{~mol}^{-1} \\ & \mathrm{~s}^{-1} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| (i) $\mathrm{R}=p-\mathrm{MeO}$ | 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) $\mathrm{R}=\mathrm{H}$ | 25.2 | 2.95 | 0.16 | 3.6 |
|  |  | 5.50 | 0.25 |  |
|  |  | 9.43 | 0.40 |  |
|  | 36.7 | See Fig. 2 |  | 11 |
|  | 43.5 | 1.69 | 0.48 | 23 |
|  |  | 5.02 | 1.25 |  |
|  |  | 7.88 | 1.9 |  |
| (iii) $\mathrm{R}=p-\mathrm{NO}_{2}$ | 25.1 | 2.95 | 0.11 | 1.15 |
|  |  | 5.89 | 0.15 |  |
|  |  | 10.6 | 0.20 |  |
|  | 36.7 | See Fig. 2 |  | 5.3 |
|  | 43.9 | 2.95 | 0.69 | 13 |
|  |  | 7.88 | 1.35 |  |

(b) Effect of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left(\mathrm{R}=\mathrm{H} ; T=25^{\circ} \mathrm{C} ;\left[\mathrm{Tl}^{3+}\right]=5.54 \times 10^{-3} \mathrm{~mol}\right.$ $\mathrm{dm}^{-3}$; ionic strength $=0.99 \mathrm{~mol} \mathrm{dm}^{-3}$ ).

| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] / \mathrm{mol} \mathrm{dm}^{-3} k_{\text {obs }} / 10^{-4} \mathrm{~s}^{-1}$ |  |
| :--- | :--- |
| 0.28 | 0.41 |
| 0.40 | 0.40 |
| 0.96 | 0.38 |

(c) Effect of ionic strength, $I\left(\mathbf{R}=\mathbf{H} ; T=25^{\circ} \mathrm{C} ;\left[\mathrm{Tl}^{3+}\right]=5.54 \times 10^{-3}\right.$ $\mathrm{mol} \mathrm{dm}{ }^{-3} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.40 \mathrm{~mol} \mathrm{dm}^{-3}$ ).

| $I / \mathrm{mol} \mathrm{dm}^{-3}$ | $k_{\text {obs }} / 10^{-4} \mathrm{~s}^{-1}$ |
| :--- | :--- |
| 0.43 | 0.23 |
| 0.68 | 0.30 |
| 0.99 | 0.40 |

${ }^{a}\left[\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}\right]_{\text {initial }}=2-5 \times 10^{-5} \mathrm{~mol} \mathrm{dm}{ }^{-3}$; for $k_{\text {obs }}$ see Table $1 ; k=$ second-order rate constant from the slope of plot of $k_{\mathrm{obs}} v s .\left[\mathrm{Tl}^{3+}\right]$.
$\mathrm{Tl}^{3+}$ ions are found to have comparable reactivities as promoters, ${ }^{6}$ whereas in the present system $\mathrm{Tl}^{3+}$ ions are $c a$. $5 \times 10^{2}$ to $10^{3}$ fold less effective than are $\mathrm{Hg}^{2+}$ ions. $\mathrm{Tl}^{3+}$ ions have a similar, or even lower, reactivity than $\mathrm{Ag}^{+}$ions in this reaction ${ }^{2}$, a very unusual situation.
There are two other features of the results with $\mathrm{Tl}^{3+}$ 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 $k_{\text {obs }}$ axis in plots such as those in Fig. 2. Mostly $k_{\text {obs }}$ for the spontaneous reaction is $<10^{-5} \mathrm{~s}^{-1}$; the $p-\mathrm{NO}_{2}$ 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 $\mathrm{Hg}^{2+}$ and $\mathrm{Tl}^{3+}$ ion promotion, the pattern of activation parameters is very different (Table 3). More dramatic variations are found with $\mathrm{Tl}^{3+}$ ions, but the changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ largely compensate each other. It is noticeable that for the least reactive compound ( $\mathrm{R}=\mathrm{NO}_{2}$ ) $\Delta S^{\ddagger}$ is positive. These trends, and the low reactivity of $\mathrm{Tl}^{3+}$ ions in this reaction, suggest to us that $\mathrm{Tl}^{3+}$ 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 $\mathrm{RC}_{6} \mathrm{H}_{4} \mathrm{NCS}^{a} / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \quad \Delta H^{\ddagger} / \mathrm{kJ} \mathrm{mol}^{-1} \quad \Delta S^{\ddagger} / \mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$

| (i) $\mathrm{Hg}^{2+}$ ion promotion |  |  |  |
| :--- | :---: | :---: | :---: |
| $p-\mathrm{NO}_{2}{ }^{b}$ | 1.45 | $56 \pm 2$ | $-53 \pm 4$ |
| H | 3.8 | $52 \pm 2$ | $-58 \pm 2$ |
| $p-\mathrm{MeO}$ | 4.8 | $52 \pm 2$ | $-56 \pm 2$ |
| $o-\mathrm{Me}$ | 1.6 | $52 \pm 2$ | $-67 \pm 2$ |
| (ii) $\mathrm{Tl}^{3+}$ ion promotion |  |  |  |
| $p-\mathrm{NO}_{2}$ | $1.15 \times 10^{-3}$ | $99 \pm 6$ | $30 \pm 10$ |
| H | $3.6 \times 10^{-3}$ | $78 \pm 3$ | $-30 \pm 4$ |
| $p-\mathrm{MeO}$ | $8.2 \times 10^{-3}$ | $63 \pm 5$ | $-74 \pm 8$ |

${ }^{a}$ Second-order rate constant at $25.1 \pm 0.1^{\circ} \mathrm{C} .{ }^{b}$ Ref. 2.
the metal ion when forming the adduct with the substrate. This can lead to large positive values of $\Delta S$ for adduct formation, and $\Delta H$ tends to be less negative. We suggest such an effect could underlie the trend in the activation parameters for the $\mathrm{Tl}^{3+}$ ion reactions. If we assume a mechanism for $\mathrm{Tl}^{3+}$ ion promotion [eqns. (5)-(7)], analogous to that suggested for $\mathrm{Hg}^{2+}$ ions, then $k_{\mathrm{obs}}=k_{\mathrm{T} 1} K_{\mathrm{T} 1}\left[\mathrm{Tl}^{3+}\right]$. The observed activation parameters will contain a contribution from both steps (5) and (6). An especially large positive $\Delta S$ value for step (5) with the $p-\mathrm{NO}_{2}$ derivative may account for the overall positive $\Delta S^{\ddagger}$ value in this case, even if $\Delta S^{\ddagger}$ for step (6) is negative. Another feature of the results that suggests the relatively low reactivity of $\mathrm{Tl}^{3+}$ ions in these hydrolyses arises from their difficulty in forming adducts III with isothiocyanates, is the larger effect of ionic strength on $k_{\text {obs }}$ than with $\mathrm{Hg}^{2+}$ or $\mathrm{Ag}^{+}$ion promotion: we have always found that

$\left[\mathrm{Tl}^{3+}\right] / 10^{-3} \mathrm{~mol} \mathrm{dm}{ }^{-3}$
Fig. 2 Dependence of $k_{\text {obs }}$ on [ $\mathrm{Tl}^{3+}$ ] (a): p-OMe (35.5 ${ }^{\circ} \mathrm{C}$ ); $(b): p-\mathrm{H}$ (36.7 ${ }^{\circ} \mathrm{C}$ ); (c): $p-\mathrm{NO}_{2}\left(36.7^{\circ} \mathrm{C}\right)$
increases in the ionic strength accelerate soft metal ion promoted reactions when the pre-equilibria lie well to the left. ${ }^{6}$ Our comparisons of $\mathrm{Hg}^{2+}$ and $\mathrm{Tl}^{3+}$ ion promotion in other contexts ${ }^{6}$ suggests that for $\mathrm{Tl}^{3+}$ ions to exhibit a reactivity comparable to that of $\mathrm{Hg}^{2+}$ ions a chelating substrate may be required.


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