The Kinetics and Mechanisms of the Hydrolyses of 1,3-Oxathiolanes and 1,3-Dithiolanes promoted by Mercury(II) and by Thallium(III) Ions, including the Effects of pH and Added Anions

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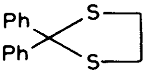
The kinetics of the mercury(II) ion-promoted hydrolysis of 2,2-diphenyl-1,3-oxathiolane (2) and of 2-phenyl-1,3-dithiolane (4) and of the thallium(III) ion-promoted hydrolysis of 2-phenyl-1,3-oxathiolane (3) and of (4), have been studied at various pH values and ambient anion concentrations using dioxane–water solvents. In the absence of the metal ion the hydrolyses are relatively slow. The mercury-promoted hydrolysis of (2) involves complex kinetic dependencies upon $[Hg^{2+}]$ and $[H_3O^+]$ and upon the concentrations of added anions. The results support the tentative mechanism previously proposed for the mercury-promoted hydrolysis of (3) which involves at pH > 3 the slow intramolecular attack of mercury-bound aquo species on the C(2) atom of the rapidly formed 1 Hg^{2+} : 1 *O,S*-acetal adduct (5). For (2), the extra phenyl group reduces the importance of a route found for (3) at pH < 3 which involves the *O*-protonation of (5). Also for (2) large values of $[Hg^{2+}]$ can lead to a change from the rate-determining hydrolysis of the Hg^{2+}–*O,S*-acetal adduct to the rate-determining hydrolysis of the resulting *O,O*-hemiacetal.The pattern of pH and anion effects found for the mercury(II) ion-promoted hydrolysis of (4) differ completely from those found for (2) and (3). They suggest a simple mechanism involving only a rate-determining intermolecular attack by water on the 1 Hg^{2+} : 1 *S,S*-acetal adduct (formation constant, *K* 4.3×10^3 l mol^{-1}). The neutralisation of one positive charge on this adduct leads to a loss of reactivity of *ca.* 25%; neutralisation of both leads to a great reduction in hydrolysis rate. The thallium(III) ion-promoted hydrolysis of (4) is mechanistically similar to the mercury reaction; the 1 : 1-adduct is less easily formed (*K* 2.9×10^2 l mol^{-1}) but reacts *ca.* 10-fold faster with water. The kinetic form of the thallium-promoted hydrolysis of (3) is especially simple: zero order in $[Tl^{3+}]$ and first-order in $[H_3O^+]$. It is argued that this should not be interpreted as implying rate-determining hemiacetal hydrolysis for this system.

Little kinetic work concerns the metal ion-promoted hydrolyses of thioacetals.[1] During our studies using aqueous alcohol and aqueous dioxane solutions we have reported [2-4] on the influence of thallium(III) ions with 2,2-diphenyl-1,3-dithiolane (1) and with 2,2-diphenyl-1,3-oxathiolane (2) and of mercury(II) ions with 2-phenyl-1,3-oxathiolane (3). Striking differences in behaviour were found. We report now on the effects of mercury(II) ions in promoting the hydrolyses of (2) and (4) and of thallium(III) ions with (3) and (4). The effects of pH changes and of added anions are also described.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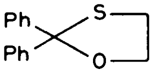
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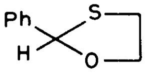
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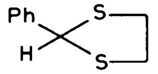
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Experimental

Compounds (2) and (3) were prepared, purified, and characterised as before; [2,3] (4) was prepared by the method [2] used for (1), but starting from benzaldehyde. It has b.p. 96 °C at 0.17 Torr. Microanalysis and the n.m.r. spectrum confirmed the product as (4). Our kinetic and other procedures for studying the hydrolyses were as previously described.[2,3] Only dioxane–water solvents were used in the present work. As before, the metal ion-promoted hydrolysis led to excellent yields of benzophenone [(1) and (2)] and benzaldehyde [(3) and (4)]. The rates of the spontaneous or purely hydrogen ion-catalysed hydrolyses of these *S*-acetals were always negligible compared with the metal-promoted rates. Values of k_{obs}, the observed first-order rate constant, were reproducible to within ±6%. Typical results, including the concentration, temperature, and other conditions used, are in the Tables and Figures.

Results and Discussion

Mercury(II) *Ion-promoted Hydrolysis of* (2).—Our results for this system are in Figures 1—3. The complex kinetic pattern is in most respects similar to that found [3,4] for the structurally related *O,S*-acetal (3). There are, however, two significant differences. First, instead of the smooth increase in k_{obs} to a steady maximum value as $[Hg^{2+}]$ is increased under otherwise fixed conditions, we find for (2) two opposing effects on k_{obs} (Figure 1). Whereas all the kinetic features of the

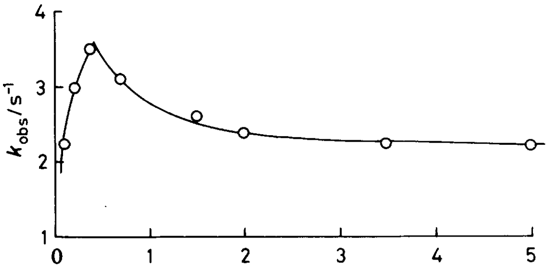
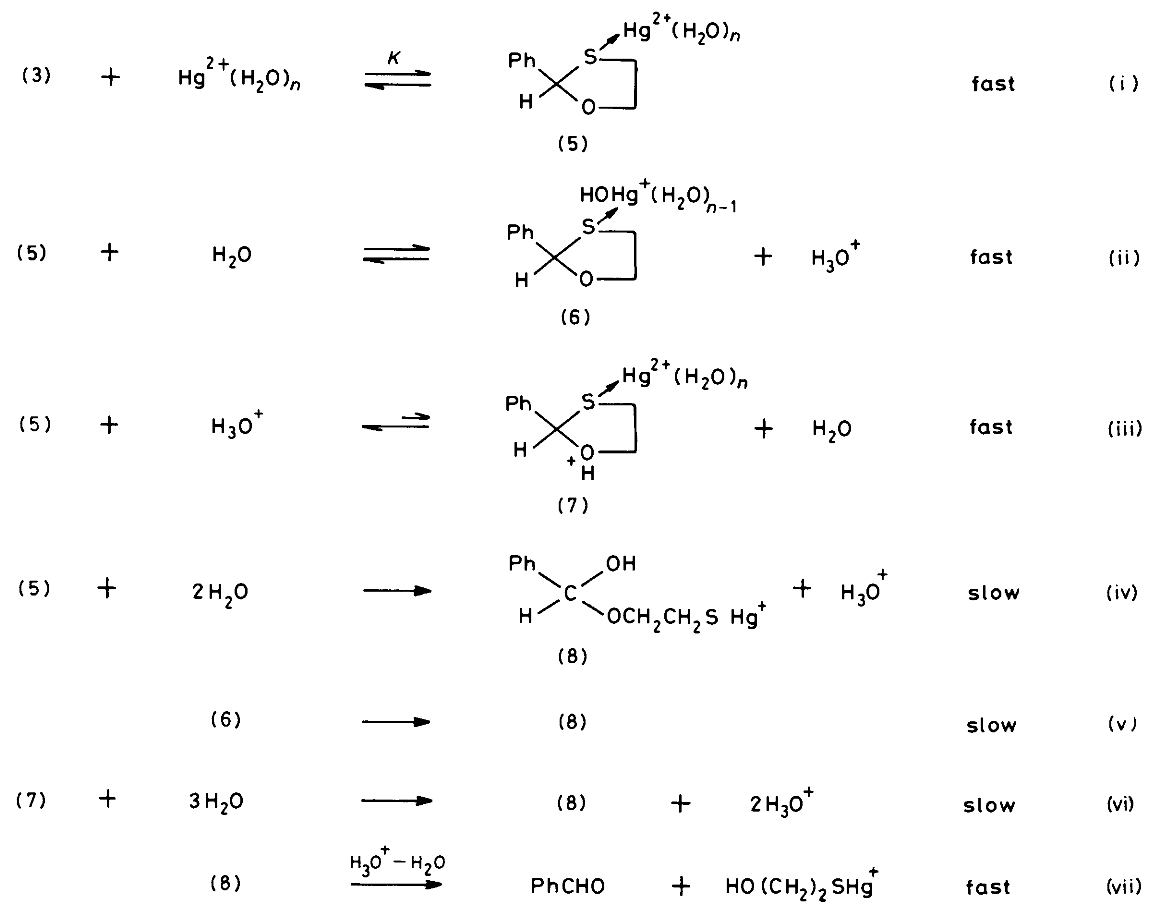
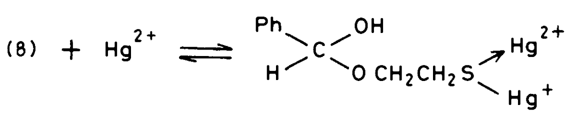


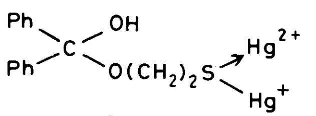
Figure 1. Dependence of the hydrolysis of 2,2-diphenyl-1,3-oxathiolane (2) on $[Hg_2^+]$. $[(2)]_{init}$ 2×10^{-5}M; $[H_3O^+]$ 0.05M; ionic strength 0.20M; solvent 10% (v/v) dioxane–water; temperature 25 °C



Scheme 1. For simplicity some of the co-ordinated water molecules are omitted



(9) (viii)



(10)

hydrolysis of (3) can be explained [3,4] by the mechanism outlined in Scheme 1, such a Scheme cannot account for the effects illustrated in Figure 1.

An important assumption of Scheme 1 is that the *O,O*-hemiacetal (8) hydrolyses more rapidly under the prevailing conditions than do (5)—(7). On moving from (3) to (2) the replacement of hydrogen by a phenyl group at the 2-position will have opposing effects, under given conditions, on the cleavage of the oxathiolane [there may be less of the species corresponding to (5), but the slow steps will be accelerated]; the rate of the hydrogen ion-catalysed hydrolysis of the hemiacetal is likely, however, to be decelerated. Also past experience [5] shows that when Hg^{2+} is attached to a sulphur anion [as *e.g.*, in (8)] a further Hg^{2+} ion can be added to give a 2 Hg^{2+} : 1 RS^- adduct. If (8) is progressively converted into (9) as $[Hg^{2+}]$ is increased, this would be expected (for electrostatic reasons) to make its hydrogen ion-catalysed hydrolysis more difficult. For (8) we assume this effect is insufficient to make hemiacetal hydrolysis the slow phase of the overall hydrolysis, but starting with the diphenyloxathiolane (2) this additional deceleration may well be sufficient, at high values of $[Hg^{2+}]$, to render the hemiacetal hydrolysis rate determining. We suggest therefore that the results in Figure 1 can be interpreted as evidence for a change in the rate-determining step of the hydrolysis of (2) as $[Hg^{2+}]$ is increased. And we interpret the final, steady value of k_{obs} in Figure 1 as the rate constant for the hydrolysis of (10) under the given conditions.

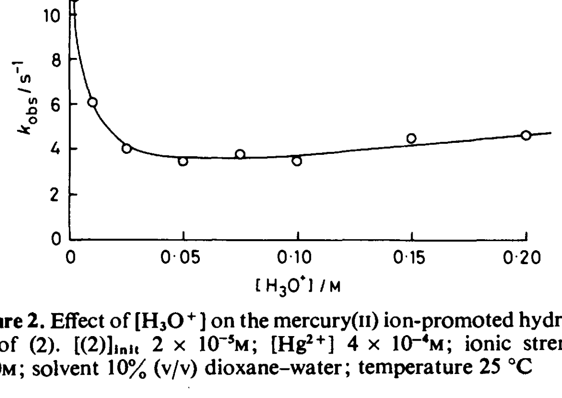


Figure 2. Effect of $[H_3O^+]$ on the mercury(II) ion-promoted hydrolysis of (2). $[(2)]_{init}$ 2 × 10^{-5}M; $[Hg^{2+}]$ 4 × 10^{-4}M; ionic strength 0.20M; solvent 10% (v/v) dioxane–water; temperature 25 °C

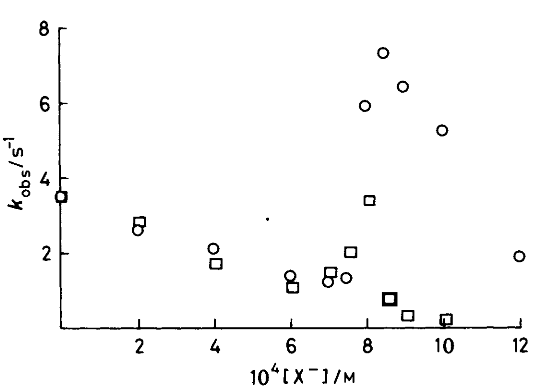


Figure 3. Effects of added anions on the mercury(II) ion-promoted hydrolysis of (2). $[(2)]_{init}$ 2 × 10^{-5}M; $[Hg^{2+}]$ 4 × 10^{-4}M; $[H_3O^+]$ 0.05M; ionic strength 0.20M; solvent 10% (v/v) dioxane-water; temperature 25 °C; ○ = Cl^-, □ = SCN^-

Table 1. Mercury(II) ion-promoted hydrolysis of (4)

$[(4)]_{initial} \simeq 1 \times 10^{-5}$M; ionic strength 0.20M; solvent 1% (v/v) dioxane-water; t_p 25.0 °C, except as stated; for k_{obs} see text

(a) Effect of $[Hg^{2+}]$ ($[H_3O^+]$ 0.05M)
See Figure 4

(b) Effect of $[H_3O^+]$ ($[Hg^{2+}]$ 4.0 × 10^{-4}M)

$10^4[H_3O^+]$/M	0.50	2.0	5.0	10	100	500	1 500
k_{obs}/s^{-1}	0.33	0.34	0.35	0.39	0.40	0.40	0.38

(c) Effect of $[Cl^-]$ ($[Hg^{2+}]$ 4.0 × 10^{-4}M; $[H_3O^+]$ 0.05M)
See Figure 5

(d) Effect of temperature ($[Hg^{2+}]$ 1.0 × 10^{-3}M; $[H_3O^+]$ 0.05M)

t_p/°C	14.3	25.0	38.6
k_{obs}/s^{-1}	0.18	0.50	1.6

E_a 60 ± 3 kJ mol^{-1}; $\Delta S^\ddagger$ −40 ± 6 J K^{-1} mol^{-1}

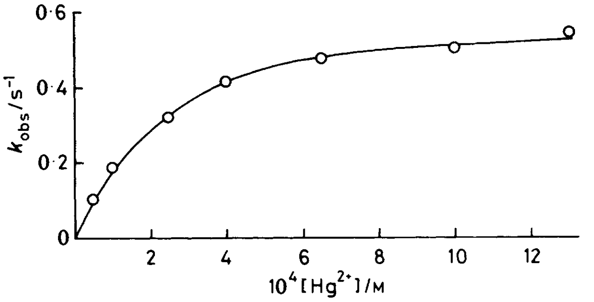


Figure 4. Dependence of the hydrolysis of 2-phenyl-1,3-dithiolane (4) on $[Hg^{2+}]$. $[(4)]_{init}$ 1 × 10^{-5}M; $[H_3O^+]$ 0.05M; ionic strength 0.20M; solvent 1% (v/v) dioxane-water; temperature 25 °C

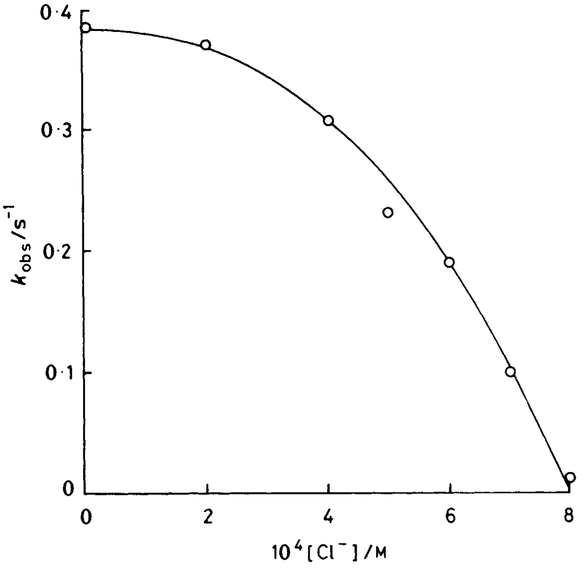
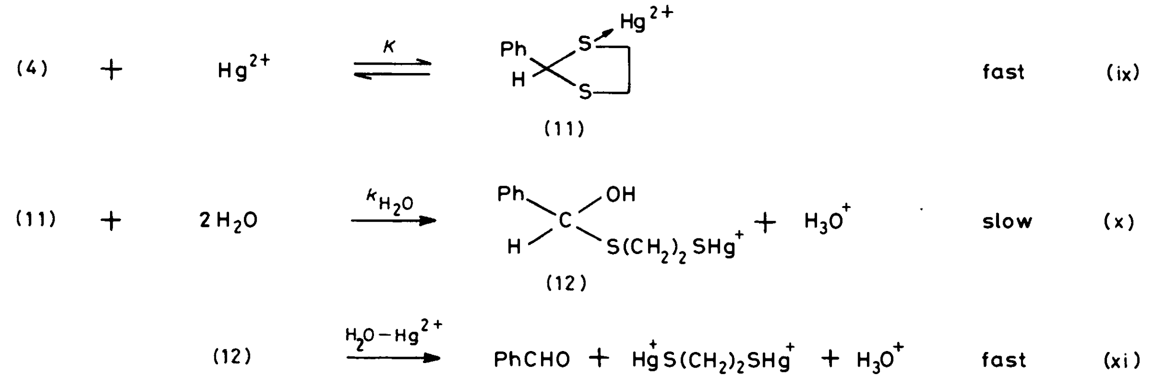


Figure 5. Effect of added chloride ions on the mercury(II) ion-promoted hydrolysis of (4). $[(4)]_{init}$ 1 × 10^{-5}M; $[Hg^{2+}]$ 4 × 10^{-4}M; $[H_3O^+]$ 0.05M; ionic strength 0.20M; solvent 1% (v/v) dioxane-water; temperature 25 °C

If we accept the foregoing interpretation then, since the other kinetic results for (2) were obtained (Figures 2 and 3) at a value of $[Hg^{2+}]$ where hemiacetal hydrolysis has not yet become rate determining, it is reasonable to expect them to show effects similar to those found[3,4] for compound (3). This is especially the case for the effects of added anions (Figure 3) because the anions are expected to accelerate the hydrolysis of the hemiacetal at all concentrations by reducing the charge on the metal. It is significant therefore that the results in Figure 3 are similar in pattern to those obtained[4] with (3). Figure 2 reveals that the pH effects for (2) and (3) are also similar, except that the hydrogen ion-catalysis found at low pH is much less prominent for (2). This is the second significant difference between the kinetics of compounds (2) and (3); we attribute it to the presence of the second phenyl group in (2) making the equilibrium analogous to equilibrium (3) less favourable for (2). A detailed (quantitative) interpretation of the pH profile for (3) in terms of Scheme 1 is given in ref. 3 where it is shown how equilibrium (iii) and step (vi) can underlie the hydrogen ion-catalysis observed at low pH. A similar quantitative analysis for compound (2) does not seem justified owing to the greater complexity of its hydrolysis, although we assume that (2) and (3) enjoy essentially analogous mechanisms when $[Hg^{2+}] \lesssim 4.5 \times 10^{-4}$M. Numerical comparisons between the rate constants found for (2) and (3) are complicated by the somewhat different solvent compositions used for the two compounds (dictated by solubility requirements). The relative values of k_{obs} found for the two compounds are, however, qualitatively compatible with the foregoing discussion of mechanism. We believe that our original tentative interpretation of the results for (3) in terms of Scheme 1 is reinforced by the even more complex behaviour now reported for (2).

Mercury(II) *Ion-promoted Hydrolysis of* (4).—Our results for this system are in Table 1 and Figures 4 and 5. The contrast with the results for compound (2) is striking; the more relevant comparison is, however, with our previous[3] results for (3). For both substrates (3) and (4) at relatively high hydrogen ion concentrations and at fixed ionic strength, increases in $[Hg^{2+}]$ lead to smooth increases in k_{obs} to steady, maximum values (*e.g.*, Figure 4). The effects are compatible with the existence of rapid 1 : 1 pre-equilibria between the substrate molecules and mercury(II) ions [equilibria (1) and (9)]. If we write an outline mechanism for the hydrolysis of (4) as equilibrium (ix) together with reactions (x) and (xi), then the expected rate equation is (xii). The results in Figure 4 are well fitted by equation (xii) with K 4.3 × 10^3 l mol^{-1} and k_{H_2O} 0.62 s^{-1}. These values are quite similar to those obtained[3] for the analogous reactions of compound (3) and suggest therefore that the mercury ions in the adducts (5) and (11) are not chelated.



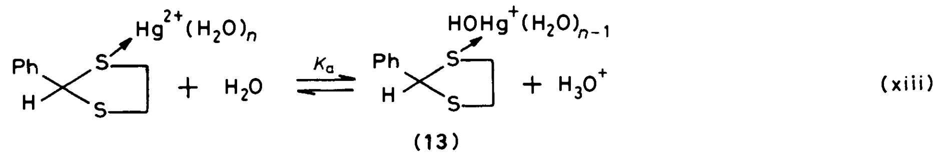
$$d[PhCHO]/dt = k_{H_2O}[(11)]$$
$$\therefore\ k_{obs} = k_{H_2O}K[Hg^{2+}]/(1 + K[Hg^{2+}]) \quad (xii)$$

The comparable values of K and k_{H_2O} found for compounds (3) and (4) is the limit of their similarities in behaviour: changes in pH or in ambient chloride ion concentration, under otherwise fixed conditions, have very different consequences for k_{obs} for the two compounds [*cf.* Figures 5 and Table 1 with Figures 2 and 4 in ref. 3 or with Figures 2 and 3 referring to compound (2)]. As outlined above (Scheme 1) and as previously justified in detail,[3,4] we believe that the high ($\gtrsim 3$) pH and chloride ion effects found for (2) and (3) arise from the at least partly intramolecular nature of their hydrolyses, the intramolecular routes being especially facilitated at high pH or when added anions reduce the positive charge on the mercury atom to zero. It is clear that such intramolecular routes, if real, are not operating for compound (4), presumably because the presence in (4) of two (large) sulphur atoms adjacent to C(2) makes intramolecular transfer difficult. The large negative value of $\Delta S^{\ddagger}$ also argues against intramolecularity (Table 1). The hydrogen ion catalysis evident for (3), and to a lesser extent for (2), at low pH is also absent for (4) (Table 1). We attribute this fact to the replacement of the oxygen atom in (5) by the sulphur atom in (11): in solution sulphur is much more difficult to protonate than oxygen.[5]

In fact the pH and chloride ion effects found for (4) are nicely compatible with the simple mechanism [equations (ix)—(xi)] proposed above on the basis of the effects of the mercury(II) ion concentration. In such a mechanism any loss of positive charge on the promoting ion will be expected to reduce k_{obs} by reducing both K and k_{H_2O}. Addition of chloride ions to a solution containing Hg^{2+} ions leads progressively to $HgCl^+$, $HgCl_2$, $HgCl^{3-}$, and $HgCl_4^{2-}$. The first two equilibria have very large association constants [6] so that uptake of Cl^- is effectively quantitative until $[Cl^-] \gtrsim 2[Hg^{2+}]$. The curve in Figure 5 therefore suggests that $HgCl^+$ is only slightly (*ca.* 25%) less reactive than is Hg^{2+}, but that $HgCl_2$ is relatively very unreactive (when the hydrolysis is intermolecular). This result is in accordance with previous findings.[5] So far as the pH effects are concerned, the K_a value [3] for equilibrium (ii) is *ca.* 8×10^{-4}; it is probably similar when [equation (xiii)] the *S*-acetal is (4). The results in Table 1 could therefore imply that the reactivity of (13) is *ca.* 20% less than that of (11). If so this way of reducing the charge on mercury has roughly the same effect as the addition of one Cl^- ion. That is a sensible conclusion.

There is no reason to believe that hemiacetal species play any kinetically significant role in the mercury(II) ion-promoted hydrolysis of (4). This is understandable since the presence of the second sulphur atom means that the hemiacetal hydrolysis [equation (xi)] will also be susceptible to mercury ion-promotion which could be intramolecular.

Thallium(III) *Ion-promoted Hydrolysis of* (4).—Our results are in Table 2 and Figure 6. As for the mercury-promoted



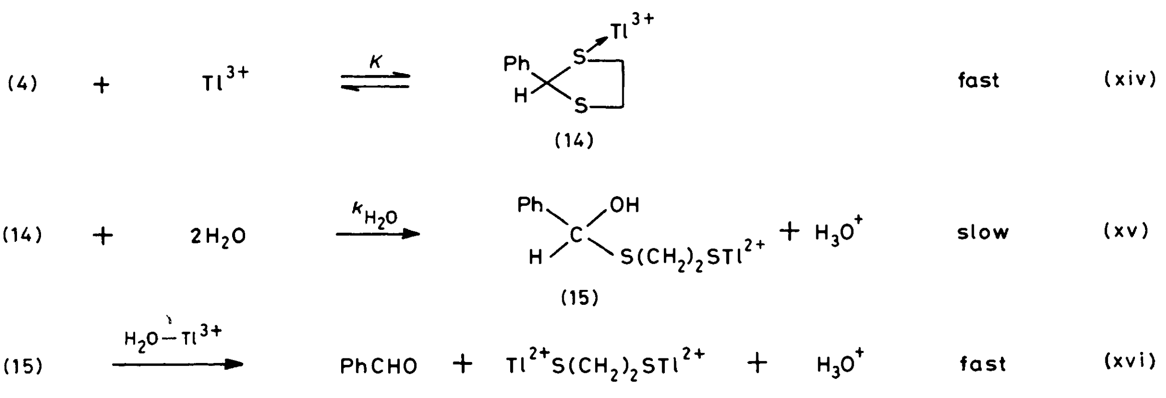


Table 2. Thallium ion-promoted hydrolysis of (4)

$[(4)]_{\rm initial} \simeq 4 \times 10^{-5}$M; ionic strength 0.50M; solvent 1% (v/v) dioxane–water; t_p 25.0 °C; for $k_{\rm obs}$ see text

(a) Effect of $[{\rm Tl}^{3+}]$ ($[{\rm H_3O^+}]$ = 0.20M)
See Figure 6

(b) Effect of $[{\rm H_3O^+}]$ ($[{\rm Tl}^{3+}]$ 4.0 × 10^{-4}M)

$[{\rm H_3O^+}]$/M	0.15	0.20	0.30	0.50
$k_{\rm obs}/{\rm s}^{-1}$	1.0	1.0	1.0	1.1

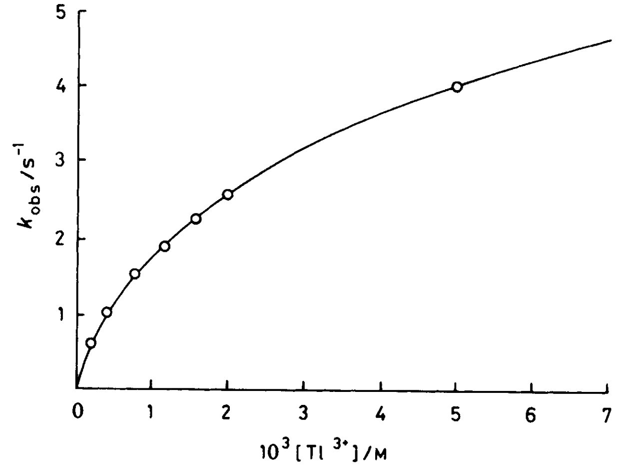


Figure 6. Dependence of the hydrolysis of (4) on $[{\rm Tl}^{3+}]$. $[(4)]_{\rm init}$ 4 × 10^{-5}M; $[{\rm H_3O^+}]$ 0.20M; ionic strength 0.50M; solvent 1% (v/v) dioxane–water; temperature 25 °C

reaction discussed above, the data suggest that the mechanism probably involves a simple scheme containing pre-equilibrium 1 : 1 adduct formation [equations (xiv)—(xvi)]. This scheme leads to equation (xvii), analogous to equation (xii), for $k_{\rm obs}$ and the results in Figure 6 are well fitted with K 290 l mol^{-1}

$$k_{\rm obs} = k_{\rm H_2O}K[{\rm Tl}^{3+}]/(1 + K[{\rm Tl}^{3+}]) \qquad ({\rm xvii})$$

and $k_{\rm H_2O}$ 7.0 s^{-1}. It follows that (14) is less easily formed than is (11) but reacts to give the hemiacetal *ca.* 10-fold more rapidly.

Previous results[2] for compound (1) with thallium(III) ions are compatible with those now obtained for (4): the extra phenyl group in (1) makes it less basic towards the metal ion so that the equilibrium corresponding to reaction (xiv) lies well to the left for (1) and $k_{\rm obs}$ displays a simple first-order dependence on $[{\rm Tl}^{3+}]$ over the concentration range involved.

Thallium(III) *Ion-promoted Hydrolysis of* (3).—Our results for this system are in Table 3 and Figure 7. The instructive comparisons here are with compounds (2) and (4). Like[2] (2), but unlike (4), compound (3) leads to $k_{\rm obs}$ values which are independent of $[{\rm Tl}^{3+}]$ in the concentration range examined (Table 3). Unlike both (2) and (4), for (3) $k_{\rm obs}$ increases with $[{\rm H_3O^+}]$ when $[{\rm H_3O^+}] \gtrsim 0.1$M at a fixed value of $[{\rm Tl}^{3+}]$ (Figure 7). For both (2) and (4) we have been led to a scheme such as equations (xiv)—(xvi) in which hemiacetal hydrolysis is relatively fast and in which, for (2), the pre-equilibrium lies to the right so that $k_{\rm obs}$ is independent of $[{\rm Tl}^{3+}]$. The results now found for (3) at first sight suggest that the slow step for this *S*-acetal is the hemiacetal hydrolysis since then $k_{\rm obs}$ would be expected[7,8] to be independent of $[{\rm Tl}^{3+}]$ but dependent on $[{\rm H_3O^+}]$, as found. However, comparison of the magnitudes of the various rate constants, bearing in mind the expected effect of the additional 2-phenyl group in (2) compared with (3), and also the known[7,9] rate of hydrolysis of the hemiacetal (16), leads us to prefer Scheme 2 for the hydrolysis of (3).

Table 3. Thallium(III) ion-promoted hydrolysis of (3)

$[(3)]_{\rm initial} \simeq 4 \times 10^{-5}$M; ionic strength 0.50M; solvent 1% (v/v) dioxane–water; t_p 25.0 °C, unless stated otherwise, for $k_{\rm obs}$ see text

(a) Effect of $[{\rm Tl}^{3+}]$ ($[{\rm H_3O^+}]$ 0.20M)

$10^3[{\rm Tl}^{3+}]$/M	0.20	0.40	0.60	1.75	2.50
$k_{\rm obs}/{\rm s}^{-1}$	30	29	30	29	32

(b) Effect of $[{\rm H_3O^+}]$ ($[{\rm Tl}^{3+}]$ = 4.0 × 10^{-4}M)
See Figure 7

(c) Effect of $[{\rm Cl}^-]$ ($[{\rm Tl}^{3+}]$ 4.0 × 10^{-4}M; $[{\rm H_3O^+}]$ 0.20M)

$10^3[{\rm Cl}^-]$/M	0	0.20	0.40	0.70	1.00	1.40	2.00
$k_{\rm obs}/{\rm s}^{-1}$	29	26	24	13	10	7.3	6.8

(d) Effect of temperature ($[{\rm Tl}^{3+}]$ 4.0 × 10^{-4}M; $[{\rm H_3O^+}]$ 0.20M)

t_p/°C	13.6	25.0	35.6
$k_{\rm obs}$./s^{-1}	12	28	55

E_a 50 ± 3 kJ mol^{-1}; $\Delta S^‡$ −58 ± 6 J K^{-1} mol^{-1}

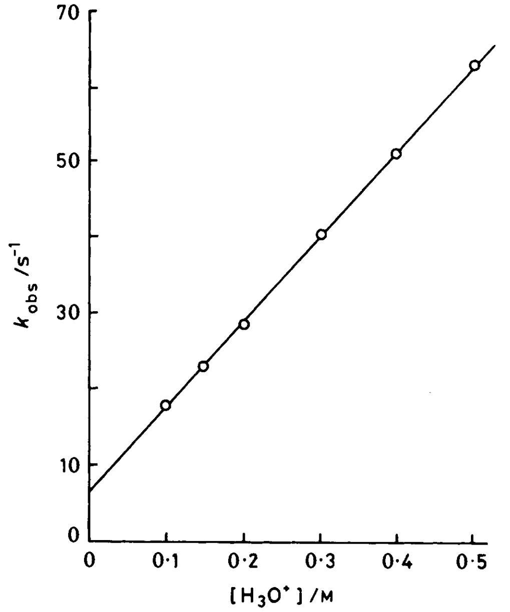
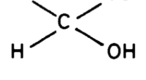
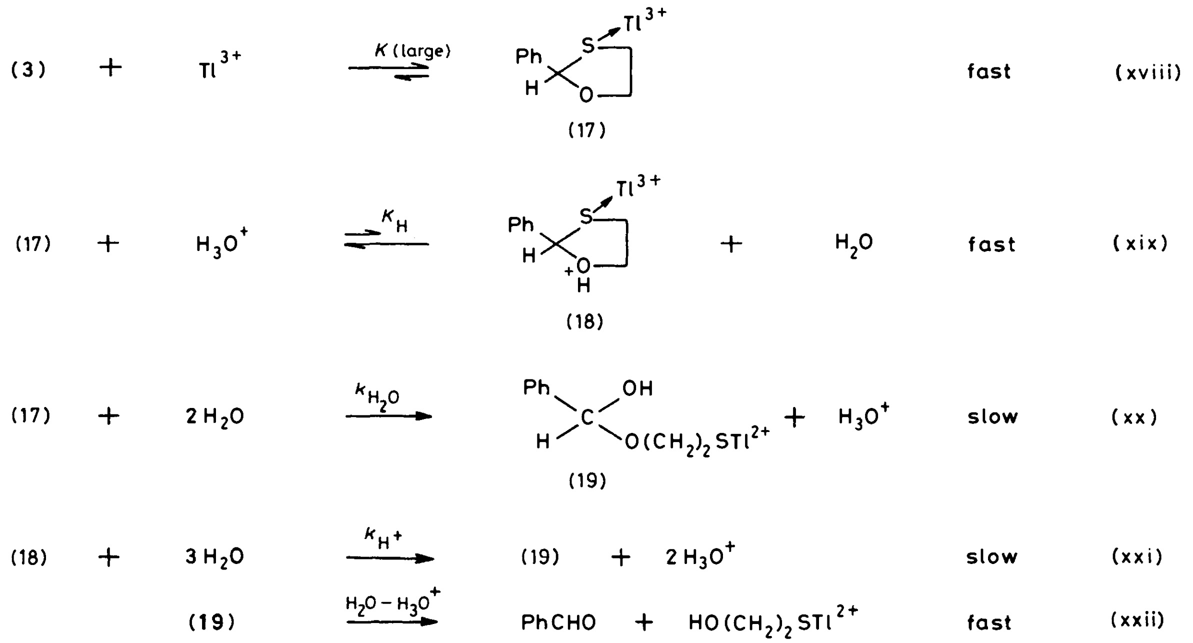


Figure 7. Effect of hydrogen ion concentration on the thallium(III) ion-promoted hydrolysis of (3)]. $[(3)]_{\rm init}$ 4 = 10^{-5}M; $[{\rm Tl}^{3+}]$ 4 × 10^{-4}M; ionic strength 0.50M; solvent 1% (v/v) dioxane–water, temperature 25 °C



(16)

Scheme 2 is also more compatible with the effects on $k_{\rm obs}$ of added chloride ions (Table 3). If the hydrolysis of (19) were the slow process, added $\rm Cl^-$ ions, by reducing the charge on (19), would be expected to *increase* $k_{\rm obs}$ since the hydrogen ion-catalysis of the *O*,*O*-hemiacetal hydrolysis would be facilitated. However, $k_{\rm obs}$ decreases with increase in $[{\rm Cl}^-]$ at all concentrations. This result is compatible with Scheme 2 on



Scheme 2.

which chloride ions will have opposing effects: they will certainly favour protonation, but they will always reduce the charge on any adduct formed and will therefore lower k_{obs}, as found.

The rate equation corresponding to Scheme 2 leads to equation (xxiii) for k_{obs}. It is interesting that the values of k_{H_2O} for (3) (6.5 ± 0.5 s^{-1}; see Figure 7 intercept) and for (4) (*ca.* 7.0 s^{-1}; see above) are the same within experimental error.

$$k_{obs} = k_{H_2O} + k_{H^+}K_H\,[H_2O^+] \qquad \text{(xxiii)}$$

This implies that (14) and (17) are attacked by water at roughly the same rate (as might be expected from the similar inductive effects of OR and SR groups [10]) although the co-ordinated Tl^{3+} ion is much more easily lost from (14) (K is much smaller). These results suggest that the surprising general finding [2] that the very soft Tl^{3+} ion attaches itself much more easily to *O,S*- than to *S,S*-acetals arises principally from a steric effect.

Finally, the fact that a contribution from hydrogen ion catalysis is found in the thallium(III) ion-promoted hydrolysis of (3) fits satisfactorily into the overall pattern. In either mercury(II) or thallium(III) ion-promotion we find that a contribution from H_3O^+ is always absent with *S,S*-acetals; its magnitude with *O,S*-acetals depends upon the electron drain upon the oxygen atom: for (3) it is substantial but for (2) it is much smaller and only detectable for the Hg^{2+}, and not for the Tl^{3+}, adduct. That is a coherent set of results.

References

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