# Kinetics and Mechanism of the Metal Ion-promoted Hydrolysis of 2-Phenyl-1,3-dithiane in Aqueous Dioxane Solution

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In 1% (v/v) aqueous dioxane the hydrolysis of 2-phenyl-1,3-dithiane (1) is promoted by thallium(III), mercury(II), mercury(I), and silver(I) ions; the qualitative sequence of their efficiencies is $Tl^{3+} \gtrsim Hg^{2+} > Hg_2^{2+} \gg Ag^+$. Kinetic studies suggest the reaction mechanism with the thallium and mercury ions involves the rapid formation of a 1:1-adduct between the metal ion and the dithiane (formation constant, K 54.5, 3.0 × 10^4, and 630 dm^3 mol^{-1} for Tl^{3+}, Hg^{2+}, and Hg_2^{2+}, respectively at 25 °C) followed by a slow ring-opening step (k_2 77, 0.20, and 0.07 s^{-1}, respectively) which may not involve water. Added chloride ions inhibit the mercury(II) ion promotion: $HgCl^+$ and $HgCl_2$ have, respectively, ca. 90% and ca. 14% of the reactivity of Hg^{2+}. An increase in the dioxane content of the solvent to 20% (v/v) has relatively little effect on the reaction. The general kinetic pattern, and level of reactivity, is similar to that observed previously for the Tl^{3+}- and Hg^{2+}-promoted hydrolyses of 2-phenyl-1,3-dithiolane (4). Both (1) and (4) are less basic towards Tl^{3+} than towards Hg^{2+}, and the thallium adducts of (1) and (4) both react more rapidly than the corresponding Hg^{2+} adducts. However, (1) is less basic than (4) towards Tl^{3+}, whereas the reverse is true for Hg^{2+}, and the Tl^{3+} adduct of (1) is more reactive than that of (4), whereas the reverse is true of the reactivities of the corresponding Hg^{2+} adducts. These differences of detail suggest that the (unknown) conformations of the adducts control to some extent the values of K and k_2.

The hydrogen ion-catalysed hydrolysis of 1,3-dithianes is extremely slow,[1] and the kinetics and mechanisms of these reactions have not been studied quantitatively. Dithianes are used as potential (or protected) carbonyl groups in various organic syntheses, and a number of mostly soft metal-based recipes are available for their hydrolysis.[2] We report now for the first time on the kinetics of some of the metal ion-promoted hydrolyses. We have used mercury(II), mercury(I), thallium(III), and silver(I) ions with 2-phenyl-1,3-dithiane (1), in aqueous 1,4-dioxane solution [equation (1)].

Ph S—
  X   ⟩ + H₂O ──M^{n+}──→ PhCHO + HS(CH₂)₃SH   (1)
H S—
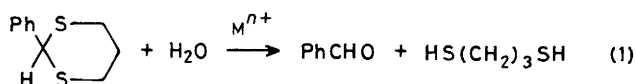
(1)

Experimental

Compound (1) was prepared from benzaldehyde and propane-1,3-diol by the method used[3] for the corresponding 1,3-dithiolane. It was recrystallised from methanol and had m.p. 71 °C. The n.m.r. spectrum established the product as (1). The sources and purification of the other materials were as in our previous work on the metal ion-promoted hydrolyses of S-compounds.[3–6] Our kinetic and other procedures for monitoring the hydrolyses also followed previous lines.[4,5] The stopped-flow method was necessary for all runs with (1) using mercury or thallium ions. The solvent was normally 1% (v/v) dioxane–water, but higher proportions of dioxane were also used for the mercury(II)-promoted reactions. All the promoted hydrolyses led to very high yields of benzaldehyde. The rates of the spontaneous and hydrogen ion-catalysed hydrolyses of (1) are negligible under the reaction conditions used. Values of $k_{obs.}$, the observed first-order rate constant, were reproducible to within ±8%. Typical results, including the concentration, temperature, and other conditions, are in the Tables and Figures.

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

$[(1)]_{initial} \simeq 5 × 10^{-6}—2 × 10^{-5}M; t_p 25.0 °C$, solvent 1% (v/v) dioxane–water, and ionic strength 0.11M, except as stated; for $k_{obs.}$ see text.

(a) Effect of $[Hg^{2+}]$ ($[H_3O^+]$ 0.10M)

See Figure 1.

(b) Effect of ionic strength ($[H_3O^+]$ 0.05M; $[Hg^{2+}]$ 1.30 × 10^{-3}M

Ionic strength/M	0.05	0.11	0.19	0.57
$k_{obs.}/s^{-1}$	0.17	0.18	0.18	0.18

(c) Effect of $[H_3O^+]$ (ionic strength 0.20M; $[Hg^{2+}]$ 1.30 × 10^{-3}M)

$[H_3O^+]/M$	0.01	0.02	0.05	0.10	0.20
$k_{obs.}/s^{-1}$	0.16	0.17	0.18	0.19	0.18

(d) Effect of $[Cl^-]$ ($[Hg^{2+}]$ 5.15 × 10^{-4}M; $[H_3O^+]$ 0.05M)

See Figure 2.

(e) Effect of temperature ($[Hg^{2+}]$ 1.30 × 10^{-3}M, $[H_3O^+]$ 0.11M)

$t_p/°C$	16.4	25.1	31.5	38.4	45.6
$k_{obs.}/s^{-1}$	0.073	0.18	0.35	0.65	1.4

$\Delta H^{\ddagger}$ 74 ± 2 kJ mol^{-1}; $\Delta S^{\ddagger}$ − 11 ± 5 J K^{-1} mol^{-1}

(f) Effect of dioxane

(i) $[Hg^{2+}]$ 3.93 × 10^{-5}M

Dioxane/% (v/v)	1.0	10.0	20.0
$k_{obs.}/s^{-1}$	0.12	0.12	0.11

(ii) $[Hg^{2+}]$ 1.90 × 10^{-3}M

Dioxane/% (v/v)	1.0	10.0	20.0
$k_{obs.}/s^{-1}$	0.19	0.18	0.16

Results and Discussion

Mercury(II) Ion-promotion.—Our results are illustrated in Table 1 and Figures 1 and 2. The effects of changes in $[Hg^{2+}]$, under otherwise fixed conditions (Figure 1), suggest that the
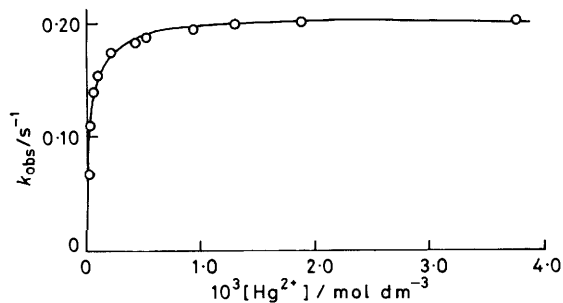
Figure 1. Effect of mercury(II) ion concentration. For conditions see Table 1
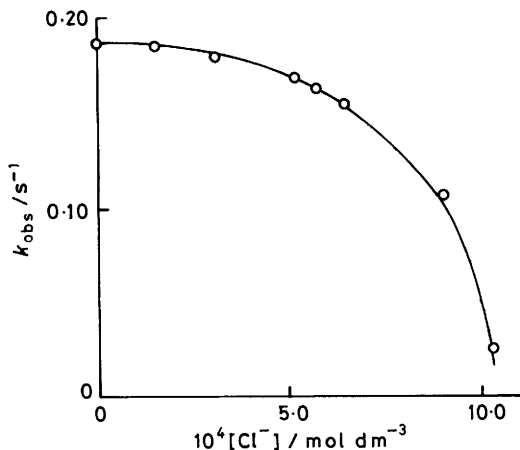

Figure 2. Effect of chloride ion concentration on mercury(II) ion promotion. $[Hg^{2+}]_{stoich} = 5.15 \times 10^{-4}$ mol dm^{-3}. For other conditions see Table 1

metal ion and (1) engage in an equilibrium leading to a 1:1-adduct (2). The outline mechanism of equations (2)—(4) is compatible with our results. The corresponding rate equation is (5), and the results in Figure 1 are well fitted (continuous curve) with $K = 3.0 \times 10^4$ dm^3 mol^{-1} and $k_2 = 0.20$ s^{-1} at 25 °C. The assumption of a relatively rapid loss of the thiohemiacetal (3), in
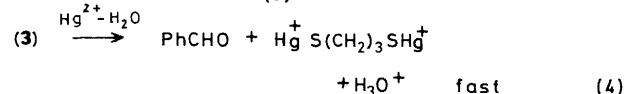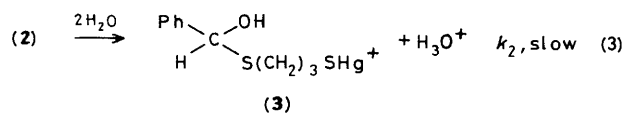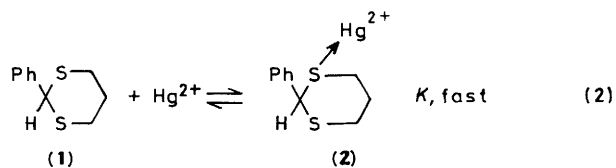
the presence of an excess of Hg^{2+} ions, is compatible with earlier results with other S,S-acetals.[3,4] The activation parameters (Table 1) were obtained at a value of $[Hg^{2+}]$ at which the pre-equilibrium (2) lies well to the right, and will reflect principally the effect of temperature on k_2; the parameters suggest[6–9] little

incorporation of free water into the transition state of step (3), and the effects of changes in $[H_3O^+]$ and $[Cl^-]$ argue against an intramolecular transfer of water from the solvation shell of the metal ion, such as that found with 1,3-oxathiolanes.[3,5] Step (3) may therefore approximate to equation (6), when the overall
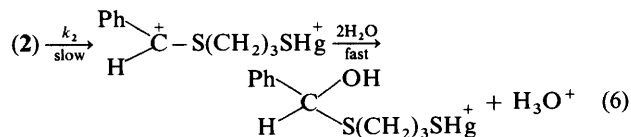
mechanism would be an analogue of the $A1$ scheme currently proposed for most hydrogen ion-catalysed hydrolyses of O,O- and O,S-acetals.[7,10] The small effect on k_{obs} of changes in ionic strength, under conditions where the equilibrium (2) lies to the right (Table 1), is in line with previous findings for analogous reactions.[4] The effects of added chloride ion (Figure 2) show[5,11] that HgCl$^+$ is only ca. 10% less effective than Hg^{2+} as a promoting ion, while the neutral HgCl$_2$ is ca. 90% less effective than Hg^{2+}.

Some of our earlier studies[4,5] with S-acetals were made with aqueous solutions containing more organic component than the 1% dioxane mostly used in the present work. To assess the effect of increasing the proportion of the organic solvent we have also examined the dithiane (1) in 10% and 20% (v/v) dioxane–water mixtures (Table 1). The effect of adding dioxane, under otherwise fixed conditions, is to slightly reduce the value of k_{obs}.

Mercury(I) *Ion-promotion.*—There exists no previous kinetic study of the effects of mercury(I) ions for any S-acetal. Our results for (1) are given in Table 2. The mercury(I) ions were added as the perchlorate.[6] In an aqueous solution of this salt there exists a disproportionation equilibrium between Hg$_2^{2+}$ and Hg^{2+} ions [equation (7)] for which,[12] under our

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg \qquad (7)$$
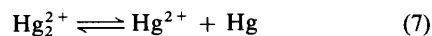
conditions, the ratio $[Hg_2^{2+}]/[Hg^{2+}] \simeq 130$. The value of k_{obs} obtained for such solutions contains therefore a contribution from the Hg^{2+} ions. This contribution can be calculated at each value of $[Hg_2^{2+}]_{stoich.}$ (using the results for Hg^{2+} ion-promotion given in the preceding section) and so the effect of the Hg$_2^{2+}$ ions can be found (Table 2; $k_{Hg(I)}$).

The general effect of an increase in $[Hg_2^{2+}]$ is similar to that found for Hg^{2+} ions, except that the mercury(I) ions are significantly less effective. Assuming a mechanism for mercury(I) ion-promotion analogous to equations (2)—(4), then $k_{Hg(I)} = k_2 K[Hg_2^{2+}]/(1 + K[Hg_2^{2+}])$. The use of $K = 630$ dm^3 mol^{-1} and $k_2 = 0.07$ s^{-1} in this equation leads to values of $k_{Hg(I)}^{calc.}$ in good agreement with the (experimental) values of $k_{Hg(I)}$ obtained from k_{obs} (Table 2). Our results show therefore that the 1:1-adduct between Hg$_2^{2+}$ and compound (1) is less stable than that involving Hg^{2+}, and also undergoes ring-scission less rapidly.

Thallium(III) *Ion-promotion.*—Our results are in Table 3 and Figure 3. Again the simple mechanism of equations (2)—(4), with Tl^{3+} in place of Hg^{2+}, suffices to explain the results. The corresponding expression for the observed rate constant is $k_{obs.} = k_2 K[Tl^{3+}]/(1 + K[Tl^{3+}])$. The experimental values of $k_{obs.}$ are well fitted (continuous curve in Figure 3) with $K = 54.5$ dm^3 mol^{-1} and $k_2 = 77$ s^{-1}. Owing to the smaller value of K, the activation parameters for the thallium system were not obtained at a thallium(III) ion concentration at which the pre-equilibrium lay far to the right. To some extent therefore they reflect the effect of temperature on K, although they should principally reflect the effect on k_2. The value of $\Delta S^{\ddagger}$ (Table 3) suggests, as for the mercury(II) ion reaction, that the slow step involves little participation of free water.

Table 2. Mercury(I) ion-promoted hydrolysis of the dithiane (1)

$[(1)]_{initial} \simeq 2 \times 10^{-5}$M; solvent 1% (v/v) dioxane–water; t_p 25 °C; ionic strength 0.11M; $[H_3O^+]$ 0.10M; for $k_{obs.}$ see text; $k_{Hg(II)}$ contribution to $k_{obs.}$ from free Hg^{2+} ions; $k_{Hg(I)} = k_{obs.} - k_{Hg(II)}$; $k_{Hg(I)}^{calc.}$ calculated from $k_2 K [Hg_2^{2+}]/(1 + K[Hg_2^+])$ using $K = 630$ dm^3 mol^{-1} and $k_2 = 0.07$ s^{-1}.

$10^4 [Hg_2^{2+}]_{stoich.}$/M	$10^6 [Hg^{2+}]$/M	$10^4 [Hg_2^{2+}]$/M	$10k_{Hg(II)}$/s^{-1}	$10k_{obs.}$/s^{-1}	$10k_{Hg(I)}$/s^{-1}	$10k_{Hg(I)}^{calc.}$/s^{-1}
2.97	2.30	2.95	0.13	0.25	0.12	0.11
4.38	3.30	4.35	0.18	0.33	0.15	0.15
5.85	4.40	5.81	0.24	0.43	0.19	0.19
9.75	7.40	9.68	0.37	0.64	0.27	0.27
14.6	11.0	14.5	0.51	0.83	0.32	0.33
24.3	18.0	24.1	0.73	1.15	0.42	0.42
29.2	22.0	29.0	0.82	1.28	0.46	0.45
48.7	37.0	48.3	1.08	1.64	0.56	0.53

Table 3. Thallium(III) ion-promoted hydrolysis of the dithiane (1)

$[(1)]_{initial} \simeq 2 \times 10^{-5}$M; solvent 1% (v/v) dioxane–water; t_p 25.0 °C; ionic strength 0.50M, except as stated; for $k_{obs.}$ see text.

(a) Effect of $[Tl^{3+}]$ ($[H_3O^+]$ 0.20M)
See Figure 3.

(b) Effect of $[H_3O^+]$ ($[Tl^{3+}]$ 3.84 × 10^{-4}M)

$[H_3O^+]$/M	0.15	0.20	0.40
$k_{obs.}$/s^{-1}	1.7	1.6	1.6

(c) Effect of ionic strength ($[H_3O^+]$ 0.20M)

(i) $[Tl^{3+}]$ 3.84 × 10^{-4}M

Ionic strength/M	0.20	0.40	0.50
$k_{obs.}$/s^{-1}	0.98	1.3	1.6

(ii) $[Tl^{3+}]$ 7.18 × 10^{-3}M

Ionic strength/M	0.40	0.62
$k_{obs.}$/s^{-1}	22.0	24.0

(d) Effect of temperature ($[Tl^{3+}]$ 4.15 × 10^{-3}M; $[H_3O^+]$ 0.20M)

t_p/°C	16.4	25.0	29.0	33.5	39.5	45.6	52.0
$k_{obs.}$/s^{-1}	7.8	14.9	17.4	24.6	35.4	56.4	82.6

$\Delta H^{\ddagger}$ 49 ± 1 kJ mol^{-1}; $\Delta S^{\ddagger}$ −13 ± 3 J K^{-1} mol^{-1}.

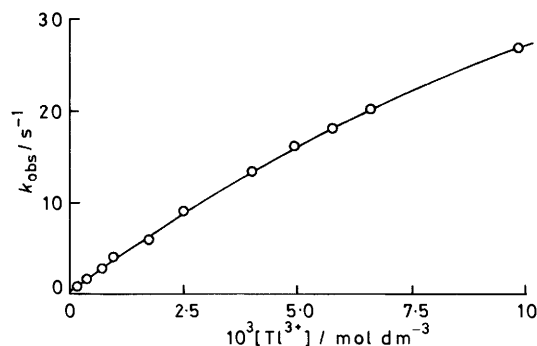**Figure 3.** Effect of thallium(III) ion concentration. For conditions see Table 3

Table 4. Mercury(II) and thallium(III) ion-promoted hydrolyses of (1) and (4)

Solvent 1% (v/v) dioxane–water; t_p 25 °C; for K (dm^3 mol^{-1}) and k_2 (s^{-1}) see text.

|	Tl^{3+}		Hg^{2+}	
(1)	K 54.5	k_2 77	K 3.0 × 10^4	k_2 0.20
(4)	K 290	k_2 7.0	K 4.3 × 10^3	k_2 0.62

The effects on $k_{obs.}$ of changes in ionic strength (Table 3) are in line with findings for other S-acetals. Thus we have previously found[4,5] that under concentration conditions when a metal ion–S-acetal adduct is only partially formed, then increasing the ionic strength leads to notable increases in $k_{obs.}$, whereas when adduct formation is more complete the effect of ionic strength on $k_{obs.}$ is smaller. This pattern is discernible in the results in Table 3.

The values of K and k_2 for Tl^{3+} show that the thallium(III) adduct with (1) is much less stable than those of mercury(I) and mercury(II), but undergoes ring-opening much more rapidly. The net effect is that thallium(III) ion-promotion is significantly faster, especially at high metal ion concentrations.

Silver(I) *Ion-promotion.*—This is relatively very inefficient compared with mercury and thallium ion-promotion. We found it too slow to study conveniently; values of $k_{obs.}$ at $[Ag^+] \simeq$ 0.1M are only *ca.* 10^{-6} s^{-1}.

Comparison with Dithiolane Hydrolysis.[3]—Kinetic results are available for the mercury(II) and thallium(III) ion-promoted hydrolyses of 2-phenyl-1,3-dithiolane, (4). So far as their general
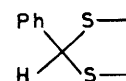
(4)

patterns of behaviour are concerned, (1) and (4) show marked similarities in both the mercury(II) and the thallium(III) ion reactions. There exist, however, significant differences of detail, and the values of K and k_2 obtained for compounds (1) and (4) are collected in Table 4.

Conformational studies of dithianes and dithiolanes suggest[1] that the geometry and immediate environment of the S-atoms in the free molecules of (1) and (4) are likely to be very similar. The results in Table 4, nevertheless, show that the two compounds display notably different basicities both towards Hg^{2+}, and towards Tl^{3+} ions. Moreover the observed effects are in opposite directions: compared with (4), compound (1) is more basic towards Hg^{2+} but less basic towards Tl^{3+}. The reactivities of the adducts also change in opposite directions: compared with the k_2 values for (4), with (1) k_2 is smaller for Hg^{2+} but larger for Tl^{3+}. These findings suggest to us that the conformations of the Hg^{2+} and Tl^{3+} adducts of the two compounds differ in some important (unknown) way or ways. This idea is supported by a comparison of the activation parameters found for mercury(II) ion-promotion: compared

with the values now found for the dithiane (Table 1), for the dithiolane[3] $\Delta H^{\ddagger}$ is smaller (62 kJ mol^{-1}) and $\Delta S^{\ddagger}$ significantly more negative (-40 J K^{-1} mol^{-1}). In both cases the parameters derive principally from the effects of temperature on the slow step (k_2). We have previously suggested for (4) that the slow step involves one or more free water molecules. It seems reasonable therefore to suggest now that the structures of the Hg^{2+} adducts of (1) and (4) may differ in a way that leads to the participation for (1) of fewer (or no) free water molecules in the ring-opening process.

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