# The Kinetics and Mechanism of the Mercurous Ion-promoted Hydrolysis of S-Thio Esters

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The kinetics of the mercurous ion-promoted hydrolysis of three p-substituted S-ethyl thiobenzoates have been studied. It has been established that the mercurous ion is a powerful soft acid with a strength lying between those of the mercuric and silver ions. The sequence of ester reactivity is p-MeO > p-H $\gg p$-NO$_2$. The substituent effects, the values of the activation parameters, and the effects of pH changes all suggest that for the p-NO$_2$ derivative the hydrolysis mechanism is $A_{Ac}2$, but that for the other two esters the mechanism is $A_{Ac}1$.

THE hydrolysis of thioesters is known to be promoted by metal ions, especially mercuric and silver ions.[1] However, so far, only one kinetic study of these reactions has been reported. Satchell and Secemski [2] examined the effect of various metal ions on the rate of hydrolysis of S-ethyl thiobenzoate, and of its p-nitro- and p-methoxy-derivatives [equation (1)]. They found that whereas

$$RC_6H_4COSEt + M^{n+} + 2H_2O \longrightarrow$$
$$RC_6H_4CO_2H + EtSM^{(n-1)+} + H_3O^+ \quad (1)$$
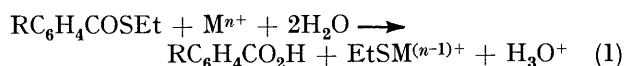
added Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} ions had little or no effect on the rate of hydrolysis in a dilute ($ca.$ 10^{-2} mol dm^{-3}) solution of hydrogen ions, Ag^+ and Hg^{2+} had a very marked effect. In the presence of these latter ions the contribution from the hydrogen ion-catalysed hydrolysis was negligible. Satchell and Secemski's results suggest that the rate-determining step in the silver ion-promoted reaction is bimolecular for all three esters, while in the mercuric ion-promoted reaction 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.

Another potentially powerful soft acid [3] which has received little attention as a catalyst is the mercurous ion. The limited information available concerning its equilibria suggests that the acidity of the mercurous ion lies between that of the mercuric and of the silver ion. For example, the equilibrium constants for 1 : 1-adduct formation with aniline are [4] 4×10^4, 5×10^3, and 28 mol dm^{-3} for Hg^{2+}, Hg_2^{2+}, and Ag^+ respectively. The efficiencies [5] of the same ions as catalysts in the hydration of nitriles co-ordinated to Co^{III} is in the sequence $Hg^{2+} > Hg_2^{2+} > Ag^+$. Again the effectiveness [6] of the ions Hg^{2+}, Hg_2^{2+}, and Tl^{3+} in displacing other metal ions from RCH_2M^{n+} is in the sequence $Hg^{2+} > Hg_2^{2+} > Tl^{3+}$, and Tl^{3+} is generally regarded [7] as a softer acid than Ag^+.

We now report a kinetic study of the mercurous-ion promoted hydrolysis of thioesters and compare our results with those of Satchell and Secemski.

EXPERIMENTAL

Materials.—All solutions were made up with freshly distilled water. AnalaR ethanol, aqueous perchloric acid (70%), and mercurous perchlorate (Agfa-Inorganics) 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 prepared by the methods described by Satchell and Secemski.[2] S-Ethyl thiobenzoate had b.p. 120—121 °C/10 mmHg (lit.,[8] 128—130 °C/12 mmHg) (Found: C, 65.3; H, 6.1; S, 18.7. Calc. for $C_9H_{10}OS$: C, 65.0; H, 6.0; S, 19.3%); $\bar{v}$(C=O) 1 670 cm^{-1}. S-Ethyl p-nitrothiobenzoate had m.p. 68.5 °C (lit.,[9] 69—70 °C); $\bar{v}$(C=O) 1 660 cm^{-1}. S-Ethyl p-methoxy-thiobenzoate had b.p. 108—109 °C/0.5 mmHg (lit.,[2] 109—110 °C/0.5 mmHg) (Found: C, 61.0; H, 6.2; S, 16.9. Calc. for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.2; S, 16.3%); $\bar{v}$(C=O) 1 660 cm^{-1}.

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 as a result contained 2% (v/v) ethanol. Stock aqueous solutions of mercurous perchlorate were made up by weight. These solutions were standardised with potassium bromide using Bromophenol Blue indicator. The flasks containing the stock mercurous perchlorate solutions and the final reaction mixtures were wrapped in aluminium foil to exclude light. Reaction mixtures were made up by volume and contained sufficient sodium perchlorate to give a total ionic strength of 0.1 mol dm^{-3}. Reaction was initiated by the final addition of a small volume of the stock ester solution. In some experiments the pH of the reaction mixtures was controlled by the addition of known amounts of perchloric acid or of sodium hydroxide. In most experiments the hydrogen ion concentration was 0.01 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 mercurous 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 log($A - A_\infty$) 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 [10] that involved an extension of the method of linear least-squares. Values of $k_{obs.}$ calculated in this way were always reproducible to within ±5%. However, for those runs in which the mercurous ion was present in less than a 10-fold excess of the ester (*i.e.* [Hg$_2^{2+}$] < 10^{-3} mol dm^{-3}) the first-order plots deviated from linearity. This deviation dis-

appeared if the ester concentration was also decreased. In these circumstances $k_{obs.}$ was obtained from the initial slope and values were reproducible to within $\pm 10\%$. For all the systems studied the contribution to the rate of hydrolysis from hydrogen ion or from solvent catalysis was negligible.

Reaction Products.—For each ester preparative-scale experiments were carried out using concentration conditions {[ester] = 5×10^{-3} mol dm^{-3}, [Hg$_2^{2+}$] = 1×10^{-2} mol dm^{-3}, [H$_3$O$^+$] = 0.1 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 >80% yield. The u.v. spectral changes observed in the kinetic runs also indicated that the products were formed in very high (ca. 100%) yield. No attempt was made to isolate the ethanethiol product. The departure from first-order behaviour when [Hg$_2^{2+}$] < 1×10^{-3} mol dm^{-3} is evidence for the removal of the mercurous ion by the ethanethiol. It seems probable that EtSHg$^+$ClO$_4^-$ is the product formed by disproportionation of EtSHg$_2^+$ClO$_4^-$.
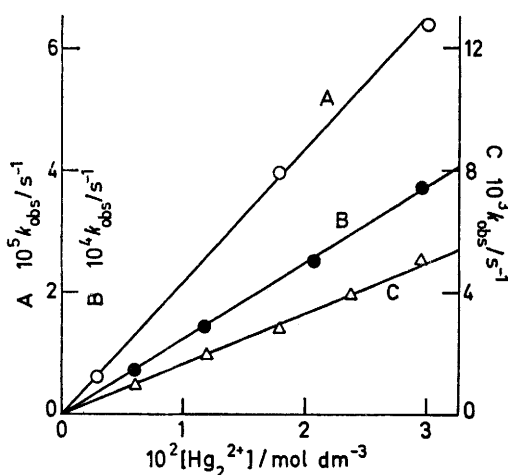

FIGURE 1 Typical plots of $k_{obs.}$ vs. [Hg$_2^{2+}$]: A = S-ethyl p-nitrothiobenzoate at 34.92 °C, B = S-ethyl p-methoxythiobenzoate at 18.56 °C, and C = S-ethyl thiobenzoate at 25.21 °C

RESULTS AND DISCUSSION

Kinetics of Hydrolysis.—Values of $k_{obs.}$ are given in Table 1. For each ester, at any fixed pH and temperature, plots of $k_{obs.}$ against [Hg$_2^{2+}$] are rectilinear and pass through the origin (Figure 1). Hence $k_{obs.}$ = k[Hg$_2^{2+}$]. Values of k obtained from the slopes of such plots are in Table 2.

Solutions of the mercurous ion also contain very low concentrations of mercuric ion owing to the disproportionation reaction (2). For this equilibrium it is

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg \qquad (2)$$

known [11] that K = [Hg$_2^{2+}$]/[Hg^{2+}] = 130. Comparison of our values for k with the corresponding values ($k_{Hg^{2+}}$) for systems containing the mercuric ion only,[2] shows that, at 25 °C, the ratio $k_{Hg^{2+}}/k$ lies between 10 and 20 for the three esters. It follows that in the present system containing both ions, the mercurous ion makes the dominant contribution to the rate. However, k will

include a contribution from the mercuric ion as in equation (3). Since [Hg$_2^{2+}$]$_{stoic}$ $\simeq$ [Hg$_2^{2+}$], it follows

$$k[Hg_2^{2+}]_{stoic} = k'[Hg_2^{2+}] + k''[Hg^{2+}]$$
$$= k'[Hg_2^{2+}] + k''[Hg_2^{2+}]/K \qquad (3)$$

TABLE 1

Selected values of $k_{obs.}$ for the mercurous ion-promoted hydrolysis of thioesters showing dependence on [Hg$_2^{2+}$]

[Ester] ca. 1×10^{-4} mol dm^{-3}, [H$_3$O$^+$] = 0.01 mol dm^{-3}, ionic strength = 0.1 mol dm^{-3}, solvent = 2% v/v ethanol–water, [Hg$_2^{2+}$] in mol dm^{-3}, $k_{obs.}$ in s^{-1}

S-Ethyl p-nitrothiobenzoate at 45.15 $\pm$ 0.10 °C

10^2[Hg$_2^{2+}$]	0.290	0.440	0.590	0.740	1.18	2.35	2.94
$10^5 k_{obs.}$	1.20	1.76	2.27	2.56	4.11	8.66	11.20

S-Ethyl thiobenzoate at 45.15 $\pm$ 0.10 °C

10^2[Hg$_2^{2+}$]	0.294	0.441	0.882	1.18	1.76	2.35
$10^4 k_{obs.}$	1.78	2.56	5.05	7.01	9.77	13.8

S-Ethyl p-methoxythiobenzoate at 35.20 $\pm$ 0.05 °C

10^2[Hg$_2^{2+}$]	0.121 *	0.302	0.362	0.604	1.51	2.90	3.02
$10^3 k_{obs.}$	1.25	3.25	3.66	6.40	15.1	29.2	30.7

* [Ester] = 2.5×10^{-5} mol dm^{-3}.

that k = $k' + k''/K$. Values of k'' for different temperatures were calculated from the results given in

TABLE 2

Values of k, k', and k''/K

See text for definitions. Values of k'' were obtained from the data in ref. 2. Units of k, k', and k''/K are mol^{-1} dm^3 s^{-1}

$t/°C$	$10^3 k$	$10^3 k''/K$	$10^3 k'$
S-Ethyl p-nitrothiobenzoate			
24.96	0.810 $\pm$ 0.048	0.086	0.724
34.92	2.19 $\pm$ 0.13	0.18	2.01
45.15	3.73 $\pm$ 0.27	0.41	3.32
60.25	11.5 $\pm$ 0.6	1.2	10.3
S-Ethyl thiobenzoate			
14.92	2.67 $\pm$ 0.14	0.19	2.48
25.21	8.26 $\pm$ 0.25	0.68	7.58
34.92	22.9 $\pm$ 1.0	2.1	20.8
45.15	58.0 $\pm$ 2.1	6.3	51.7
60.15	251 $\pm$ 11	28	223
S-Ethyl p-methoxythiobenzoate			
18.56	249 $\pm$ 10	31	218
25.21	411 $\pm$ 30	67	344
35.20	1 034 $\pm$ 45	199	835
45.40	2 393 $\pm$ 59	562	1 831

ref. 2; hence values for k' were obtained. These values (Table 2) were used to calculate the enthalpies and
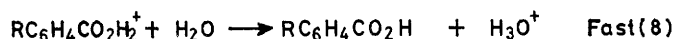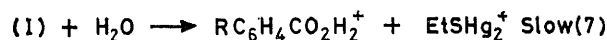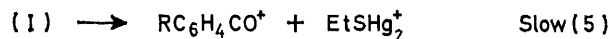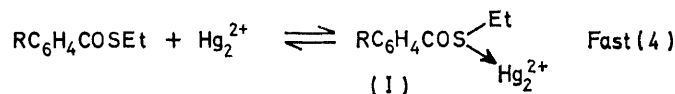
TABLE 3.

Activation parameters

$\Delta H^\ddagger$ was obtained from plots of $\ln(k'/T)$ versus $1/T$ and $\Delta S^\ddagger$ by substitution of $\Delta H^\ddagger$ into the equation $\ln(k'/T)$ = $\ln(k/h)$ $\Delta H^\ddagger/RT + \Delta S^\ddagger/R$. Units of $\Delta H^\ddagger$ are kcal mol^{-1} (kJ mol^{-1}) and of $\Delta S^\ddagger$ cal mol^{-1} K^{-1} (J mol^{-1} K^{-1})

Thiobenzoate	$\Delta H^\ddagger$ (± 1 kcal mol^{-1})	$\Delta S^\ddagger$ (± 1 cal mol^{-1} K^{-1})
S-Ethyl p-nitro-	14 (58)	−26 (−190)
S-Ethyl	18 (75)	−8 (−33)
S-Ethyl p-methoxy-	14 (58)	−13 (−54)

entropies of activation of the mercurous ion-promoted reactions (Table 3).

As with mercuric ion-promotion, the sequence of re-activity (Table 2) of the esters towards the mercurous ion is p-MeO > p-H > p-NO$_2$, this being the opposite

[equations (4)—(6)] for the p-methoxy- and p-hydrogen esters and $A_{Ac}2$ [equations (4), (7), and (8)] for the p-nitro-derivative. The product EtSHg$_2^+$ almost certainly

$$RC_6H_4COSEt + Hg_2^{2+} \rightleftharpoons RC_6H_4COS\begin{smallmatrix}Et\\ \\Hg_2^{2+}\end{smallmatrix} \qquad Fast(4)$$
$$(I)$$

$$(I) \longrightarrow RC_6H_4CO^+ + EtSHg_2^+ \qquad Slow(5)$$

$$RC_6H_4CO^+ + 2H_2O \longrightarrow RC_6H_4CO_2H + H_3O^+ \qquad Fast(6)$$

$$(I) + H_2O \longrightarrow RC_6H_4CO_2H_2^+ + EtSHg_2^+ \qquad Slow(7)$$

$$RC_6H_4CO_2H_2^+ + H_2O \longrightarrow RC_6H_4CO_2H + H_3O^+ \qquad Fast(8)$$

sequence to that found for the silver ion.[2] Also, the overall change in reactivity, a factor of ca. 470, although only about half that shown by the esters in the presence of the mercuric ion, is very much greater than that shown in the presence of the silver ion, for which the factor is ca. 20. Again, the trend in $\Delta H^{\ddagger}$ values agrees more closely with the trend found for the mercuric ion
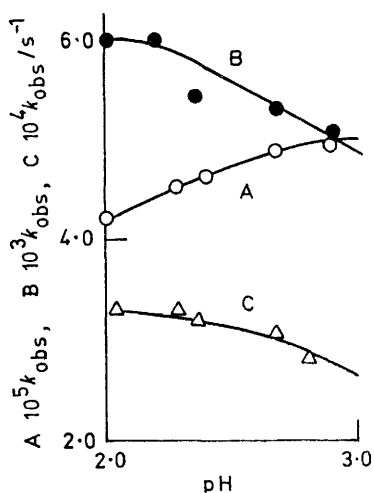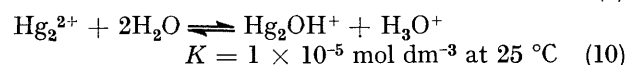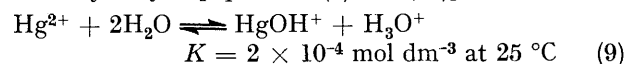

Figure 2   Effect of pH on $k_{obs.}$ with [Hg$_2^{2+}$] = 1.45 × 10^{-2} mol dm^{-3}: A = S-ethyl p-nitrothiobenzoate at 40.4 °C, B = S-ethyl p-methoxythiobenzoate at 25.2 °C, and C = S-ethyl thiobenzoate at 34.9 °C

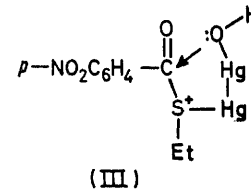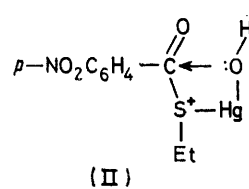than with that found for the silver ion. It is particu-larly noteworthy that, as for the mercuric ion, $\Delta H^{\ddagger}$ shows an increase from the p-nitro to the p-hydrogen ester, whereas in the case of the silver ion there is no change in $\Delta H^{\ddagger}$. Furthermore, the $\Delta S^{\ddagger}$ values, although negative for all the esters, are significantly less negative for the p-hydrogen and p-methoxy-esters than for the p-nitro-ester. Taken together these facts clearly suggest that the mechanisms underlying the mercurous ion-promotion are more similar to those underlying the mercuric ion-promotion than to those leading to silver ion-promotion. We therefore suggest for the mercurous ion-promotion the same pattern of mechanisms proposed by Satchell and Secemski[2] for the mercuric ion reactions: $A_{Ac}1$

undergoes disproportionation to give EtSHg$^+$ + Hg. Disproportionation does not occur at an earlier stage, since disproportionation of (I) would lead to the corresponding Hg^{2+}-complex, whose concentration would be controlled by the free Hg^{2+} present, and the reactions would have been slower than found.

Effect of pH.—The effect of pH changes on the value of $k_{obs.}$ is shown in Figure 2. It is known that as the hydrogen ion concentration falls from pH = 2 to 3 both the mercuric [12] and the mercurous [11] ion undergo some hydrolysis [equations (9) and (10)]. Over the same

$$Hg^{2+} + 2H_2O \rightleftharpoons HgOH^+ + H_3O^+$$
$$K = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ at } 25 °C \qquad (9)$$

$$Hg_2^{2+} + 2H_2O \rightleftharpoons Hg_2OH^+ + H_3O^+$$
$$K = 1 \times 10^{-5} \text{ mol dm}^{-3} \text{ at } 25 °C \qquad (10)$$

pH range Figure 2 shows that $k_{obs.}$ values for the p-methoxy- and p-hydrogen-derivatives decrease some-what. This decrease clearly shows that for these esters the combined reactivities of HgOH$^+$ and Hg$_2$OH$^+$ are smaller than those of Hg^{2+} and Hg$_2^{2+}$. However, for the p-nitro-ester $k_{obs.}$ increases as the pH increases. Since the contributions to $k_{obs.}$ due to Hg^{2+} and Hg$_2^{2+}$ will both be decreasing, it follows that for this ester the availability of HgOH$^+$ and/or of Hg$_2$OH$^+$ more than compensates for this decrease. Since the proposed rate-determining step in the hydrolysis of the p-nitro-derivative is normally bimolecular, these results suggest the additional importance of an intramolecular route (II) or (III) for this step when sufficient hydroxy-species are available. If the p-hydrogen and p-methoxy-esters hydrolyse *via* $A_{Ac}1$ routes, as we suggest, the

$$p-NO_2C_6H_4-\overset{\overset{O}{\parallel}}{C}\longleftarrow :O \\ \overset{|}{\underset{\underset{Et}{|}}{S^+}}-Hg \qquad\qquad p-NO_2C_6H_4-\overset{\overset{O}{\parallel}}{C}\overset{:O-H}{\diagup}\overset{}{Hg} \\ \overset{|}{\underset{\underset{Et}{|}}{S^+}}-Hg$$

$$(II) \qquad\qquad\qquad (III)$$

difference in their behaviour compared to that of the p-nitro-derivative over this pH range can readily be understood.

Comparison of the Efficiencies of Hg_2^{2+}, Hg^{2+}, *and* Ag^+ *as Promoters.*—The catalytic effectiveness of the metal ion is clearly in the sequence $Hg^{2+} > Hg_2^{2+} > Ag^+$ (Table 2 and ref. 2). Comparison for the same conditions of mechanism and temperature (*i.e. p*-nitro-ester at 25 °C) gives $k_{Hg^{2+}} : k_{Hg_2^+} : k_{Ag^+}$ as 175 : 12 : 1.

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