The Kinetics and Mechanism of the Soft Metal Ion-promoted Hydrolysis of α-Ethoxy-α-ethylthiotoluene in Aqueous Solution

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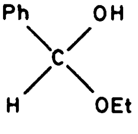
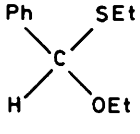
Kinetic studies show that the overall hydrolysis of the open-chain *OS*-acetal α-ethoxy-α-ethylthiotoluene in aqueous solution, promoted by mercury(II) or by thallium(III) ions, proceeds *via* rapid desulphurisation to give the hemiacetal, followed by the rate-limiting hydrogen ion-catalysed hydrolysis of the latter. With mercury(II) ions, only in the presence of relatively high concentrations of added chloride ions does the mechanism change.

We have shown[1,2] that free mercury(II) or thallium(III) ions powerfully promote the hydrolyses of various *S*-acetals in aqueous solvents of low pH. In these studies, the observed kinetics suggested mechanisms of hydrolysis *via* intermediate hemiacetals but in which, as in many proton-catalysed acetal hydrolyses,[3,4] the hydrolysis of the hemiacetal was fast and not rate-limiting. However, the rate constants found for promotion, and the known[4] rate constant for the hydrogen ion-catalysed hydrolysis of (1), suggested that, at sufficiently low hydrogen ion concentrations, the promoted hydrolysis of the open-chain *OS*-acetal (2) [equation (1)] might be limited kinetically by the rate of hydrolysis of (1). We report now on this matter.


(1)


(2)

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

EXPERIMENTAL

Materials.—Compound (2) does not appear to have been isolated previously although it has been prepared in solution.[5] It was made from αα-diethoxytoluene[6] in two stages. (i) αα-Diethoxytoluene was reacted with a mixture of acetyl and thionyl chlorides as in Straus and Heinze's procedure.[7] The resulting α-chloro-α-ethoxytoluene had b.p. 53 °C at 0.025 mmHg. (ii) The chloro-derivative was converted into (2) using Fife and Anderson's method[8] involving reaction with sodium ethanethiolate in dimethylformide. Compound (2) had b.p. 62 °C at 0.20 mmHg. N.m.r. spectra confirmed the structure and purity of (2), which contained no detectable quantities of impurities. The sources and purities of the other reagents were those given in our previous work.[1,2]

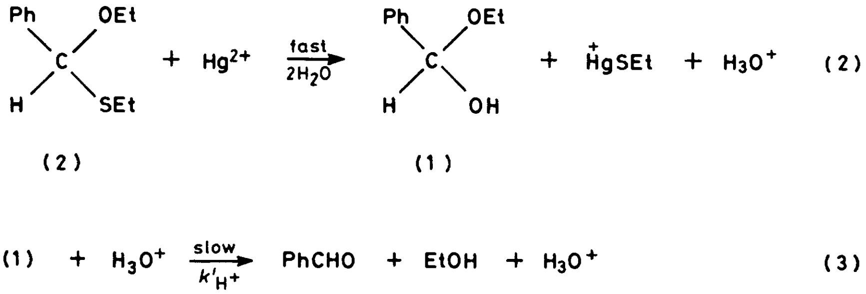
Kinetic Arrangements.—All the promoted reactions studied were relatively fast and were monitored using a stopped-flow technique.[1,2] Compounds (1) and (2) absorb weakly in the 245—290 nm region whereas the final hydrolysis product benzaldehyde, has a maximum at 250 nm and a flat shoulder at *ca.* 285 nm. For reaction mixtures containing thallium(III) ions or chloromercury ions measurements were made at 285 nm; otherwise measurements were made at 250 nm. The solvent throughout was a 1% (v/v) dioxan–water mixture and the general kinetic procedure was that used in earlier work.[1,2] Accurate first-order formation of benzaldehyde was always found and the observed first-order rate constant k_{obs} was reproducible to within ±10%. The hydrogen ion catalysis of (2) was followed by conventional u.v. spectroscopy. Under all kinetic conditions benzaldehyde was formed in quantitative yield and the reaction mixtures remained homogeneous.

RESULTS AND DISCUSSION

The Hydrogen Ion-catalysed Hydrolysis of (2).—At 25 °C in the region pH 1.0—2.0 ($HClO_4$) and ionic strength I 1.0 ($NaClO_4$) we find the catalytic constant k_{H^+} 1.45 ± 0.15 l mol^{-1} s^{-1} (*cf.* k_{H^+} 1.30 l mol^{-1} s^{-1} under similar conditions[5]). The contributions from the purely hydrogen ion-catalysed reaction to the metal ion-promoted rates were thus negligible under all the conditions used with thallium(III) and mercury(II) ions, except at very high added chloride ion concentrations (see Table).

Mercury(II) *Ion Promotion.*—Our experimental conditions and results are in Table (a). In the region pH 1.0—3.0 the hydrolysis of (2) is greatly accelerated by the presence of an excess of Hg^{2+} ions. However, under such conditions k_{obs} is independent of $[Hg^{2+}]$ but is proportional to $[H_3O^+]$; k_{obs} is also increased by an increase in ionic strength. At 25 °C and *I* 1.0, the catalytic rate constant, $k_{obs}/[H_3O^+] = k'_{H^+} = (1.1 \pm 0.1) \times 10^3$ l mol^{-1} s^{-1}. Corrected for the effect of ionic strength, this value is similar to that obtained[4] for the hydrolysis of (1) under otherwise analogous conditions. The activation parameters are E_a 51 ± 4 kJ mol^{-1} and $\Delta S^\ddagger$ −25 ± 6 J K^{-1} mol^{-1}. The value of $\Delta S^\ddagger$ (quoted wrongly in our preliminary report[9]) is somewhat more positive, and E_a is very similar, to values reported for the hydrogen ion-catalysed hydrolysis of sugar-like hemiacetals.[10] These facts all point to the Scheme for the mechanism of the Hg^{2+} ion-promoted hydrolysis of (2).

The presence of added chloride ions in the reaction mixtures does not significantly reduce k_{obs}, until relatively large $[Cl^-]/[Hg^{2+}]_{stoic}$ ratios are reached [Table (a)]. This result suggests that the species Hg^{2+}, $HgCl^+$, and $HgCl_2$ are all sufficiently powerful promoters to satisfy the Scheme. When most of the added mercury(II) ions have been converted into $HgCl_3^-$ and $HgCl_4^{2-}$ (at[11] $[Cl^-]$ 0.1M) k_{obs} falls to a value closer to that expected for the purely hydrogen ion-catalysed hydrolysis of (2). This behaviour in the presence of



SCHEME

Hydrolysis of (2) promoted by mercury(II) and thallium(III) ions. $[(2)]_{\text{initial}} = 4.0 \times 10^{-5}$M; solvent 1% (v/v) dioxan-water

(a) Mercury(II) ion promotion

(i) Effect of $[Hg^{2+}]$ ($10[H_3O^+]$ 0.50M; I 1.00M; t_p 25.0 °C)

$10^4[Hg^{2+}]$/M	1.00	2.00	4.00	5.00
k_{obs}/s^{-1}	53	54	53	55
$10^4[Hg^{2+}]$/M	20.0	50.0		
k_{obs}/s^{-1}	54	55		

(ii) Effect of $[H_3O^+]$ ($10^4[Hg^{2+}]$ 4.00M; I 1.00M; t_p 25.0 °C)

$10[H_3O^+]$/M	0.010	0.020	0.10	0.25
k_{obs}/s^{-1}	1.2	2.3	11	27
$10[H_3O^+]$/M	0.50	1.00		
k_{obs}/s^{-1}	54	113		

(iii) Effect of ionic strength ($10^4[Hg^{2+}]$ 4.00M; $10[H_3O^+]$ 0.065M; t_p 25.0 °C)

I/M	0.25	0.50	1.00	2.00
k_{obs}/s^{-1}	4.4	5.1	7.2	11.0

(iv) Effect of $[Cl^-]$ ($10^4[Hg^{2+}]$ 4.00M; $10[H_3O^+]$ 0.50M; I 1.00M)

$10^4[Cl^-]$/M	0.0	4.0	8.0	12
k_{obs}/s^{-1}	53	53	54	51
$10^4[Cl^-]$/M	24	1 000		
k_{obs}/s^{-1}	54	0.68		

(v) Effect of temperature ($10^4[Hg^{2+}]$ 4.00M; $10[H_3O^+]$ 0.017M; I 1.00M)

t_p/°C	14.0	25.0	41.0	55.0
k_{obs}/s^{-1}	0.72	1.6	4.8	13

(b) Thallium ion promotion (I 1.00M; t_p 25.0 °C)

(i) Effect of $[Tl^{3+}]$ ($[H_3O^+]$ 0.10M)

$10^4[Tl^{3+}]$/M	4.00	16.0	40.0
k_{obs}/s^{-1}	107	107	102

(ii) Effect of $[H_3O^+]$ ($10^4[Tl^{3+}]$ 4.00M)

$10[H_3O^+]$/M	0.50	1.00	1.50
k_{obs}/s^{-1}	57	107	170

added chloride ions is compatible with results obtained with 2-phenyl-1,3-oxathiolan.[2]

Thallium(III) *Ion Promotion*.—Our results are in Table (b). Less extensive, they parallel those obtained with mercury(II) ions and the observed catalytic constant k'_{H^+}, $(1.1 \pm 0.1) \times 10^3$ l mol^{-1} s^{-1}, is, within experimental error, the same. It is evident that a mechanism analogous to that in the Scheme probably also obtains for thallium(III) ion promotion.

In the past only for strained acetals has the rate of hydrolysis of the intermediate hemiacetal been found to dominate the overall hydrolysis rate.[4,10,12] Clearly, however, appropriate metal ion-promoted hydrolysis of *OS*-acetals can provide (temporary) high concentrations of the related hemiacetal free from the parent acetal. That is a circumstance which apparently occurs rather rarely in proton catalysed acetal hydrolysis.[4]

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REFERENCES

[1] D. P. N. Satchell and T. J. Weil, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1191.

[2] D. Penn and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1982, 813.

[3] E. H. Cordes and H. G. Bull, *Chem. Rev.*, 1974, **74**, 581.

[4] J. L. Jensen and P. A. Lenz, *J. Am. Chem. Soc.*, 1978, **100**, 1291.

[5] J. L. Jensen and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 1476.

[6] W. J. Hickinbottom, 'Reactions of Organic Compounds,' Longmans, London, 1957, 3rd edn., p. 238.

[7] F. Straus and H. Heinze, *Liebig's Ann. Chem.*, 1932, **493**, 191.

[8] T. H. Fife and E. Anderson, *J. Am. Chem. Soc.*, 1970, **92**, 5464.

[9] D. Penn and D. P. N. Satchell, *J. Chem. Soc., Chem. Commun.*, 1982, 54.

[10] A. L. Mori, M. A. Porzio, and L. L. Schaleger, *J. Am. Chem. Soc.*, 1972, **94**, 5034.

[11] L. G. Sillen and A. E. Martell, 'Stability Constants,' Chem. Soc. Special Publication, Nos. 17 and 25.

[12] B. Capon, *Pure Appl. Chem.*, 1977, **49**, 1001.