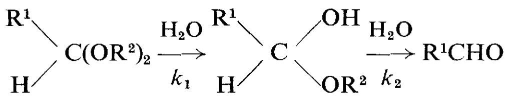
Rapid Hemiacetal Formation from a Simple, Open-chain Monothioacetal during Soft Metal Ion-promoted Hydrolysis

David Penn and Derek P. N. Satchell

Chemistry Department, King's College, Strand, London WC2R 2LS, U.K.

The Hg^{2+}- and Tl^{3+}-promoted hydrolyses of the monothioacetal α-ethoxy-α-ethylthiotoluene (**1**) proceed *via* the relatively very rapid formation of the hemiacetal (**2**) whose subsequent hydrolysis controls the observed rate of aldehyde formation.

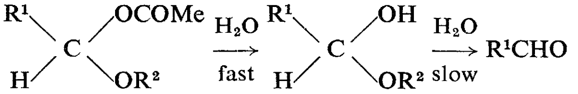
Acetal hydrolysis proceeds *via* the hemiacetal (equation 1) and, under Brønsted acid or base catalysis, normally[1,2] $k_2 \gtrsim k_1$.



$$\mathrm{R^1(H)C(OR^2)_2} \xrightarrow[k_1]{\mathrm{H_2O}} \mathrm{R^1(H)C(OH)(OR^2)} \xrightarrow[k_2]{\mathrm{H_2O}} \mathrm{R^1CHO} \qquad (1)$$

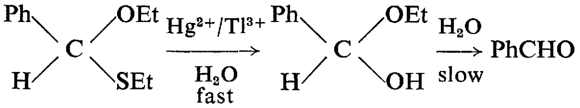
Only for certain small, cyclic, or otherwise strained acetals at acid pH has it been found that $k_1 > k_2$ and here the ratio k_1/k_2 has not been very great. The few studies[3,4] which concern metal ion-promoted hydrolysis are also compatible with $k_2 > k_1$.

Compounds which are not acetals can be prepared which, with appropriate catalysis, hydrolyse relatively very rapidly to provide a (temporary) high yield of hemiacetal in solution[5] (*e.g.* equation 2), but we have now found that soft metal



(2)

ion-promotion of the hydrolysis of simple monothioacetals such as **(1)** can lead to the same result (equation 3). The



(3)

(1) **(2)**

observed rates of benzaldehyde formation from **(1)** (5×10^{-5} M) in 1% (v/v) dioxan–water containing an excess of Hg^{2+} or Tl^{3+} ions, hydrogen ions (10^{-3} to 0·1 M) and ionic strength 1·0 M, are independent of $[Hg^{2+}]$ or $[Tl^{3+}]$ and are close to those reported[2] for **(2)**. We find $k_{H^+} = (1{\cdot}20 \pm 0{\cdot}10) \times 10^3$ dm^3 mol^{-1} s^{-1} at 25 °C using either Hg^{2+} or Tl^{3+} and $\Delta S^{\ddagger} = -58 \pm 8$ J K^{-1} mol^{-1}, a value also very close to that reported for hydrogen ion catalysis of hemiacetal hydrolysis.[6] (It was not worthwhile to confirm the expected general acid catalysis because the buffer components will interact with the metal ions and therefore render interpretation ambiguous.) There is no evidence from the kinetic data for consecutive processes with comparable rates and it is clear that in this system there occurs a very rapid removal of –SEt (as thiolate[4]) so that **(2)** is formed much faster than it is subsequently hydrolysed.

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