

## Preferential Promotion by Neutral Mercury(II) Complexes

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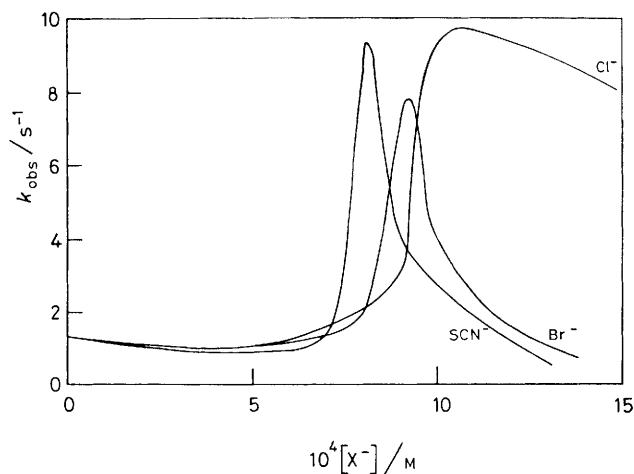
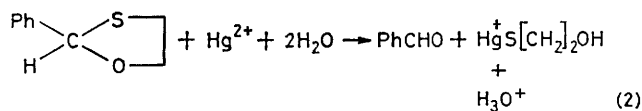
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It is shown that neutral mercury(II) species such as  $\text{HgCl}_2$  and  $\text{Hg}(\text{SCN})_2$  can be better promoters of the hydrolysis of a soft substrate than  $\text{Hg}^{2+}$  ions, an effect not found previously except with cationic substrates.

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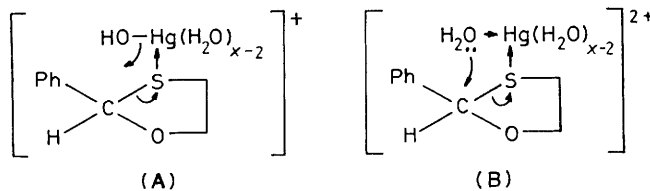
A variety of reactions in aqueous solution which involve the loss of a soft atom or group are promoted by mercury(II) ions,<sup>1</sup> for example, the aquation of inorganic complexes *via*

abstraction of halide or alkyl groups or the hydrolysis of *S*-esters or *S*-acetals. With neutral substrates it has always been found that the presence in solution of additional anions,



**Figure 1.** Dependence of  $k_{\text{obs}}$  on  $[\text{X}^-]$ .  $k_{\text{obs}}$  = observed first-order rate constant for loss of *O,S*-acetal;  $[\text{O,S-acetal}]_{\text{initial}} = 4.0 \times 10^{-5} \text{ M}$ ;  $[\text{Hg}(\text{ClO}_4)_2]_{\text{total}} = 4.0 \times 10^{-4} \text{ M}$ ;  $[\text{H}_3\text{O}^+] = 5.0 \times 10^{-2} \text{ M}$ ; ionic strength ( $\text{NaClO}_4$ ) = 1.0 M; temperature = 25.0 °C.

$\text{X}^-$ , which form complexes with  $\text{Hg}^{2+}$ , reduces the effectiveness of the promotion and the reactivity sequence  $\text{Hg}^{2+} \gg \text{HgX}^+ > \text{HgX}_2 > \text{HgX}_3^- \gg \text{HgX}_4^{2-}$  is usual.<sup>1</sup> The softer the anion  $\text{X}^-$  the more does it reduce the effectiveness of the promotion. These results reflect the fact that the Lewis acid strengths of the mercury species fall in this sequence. If the substrate carries a positive charge two opposing effects are involved: the loss of Lewis acid strength from  $\text{Hg}^{2+}$  to  $\text{HgX}_4^{2-}$  and the opposing gain in electrostatic attraction between the substrate and the mercury species. This situation can lead<sup>1</sup> to a maximum in promoting power within the sequence (*e.g.* at  $\text{HgX}_2$ ).



We have now found a similar and very striking effect of this nature but with a neutral substrate. The hydrolysis shown as reaction (1) is very powerfully promoted by  $\text{Hg}^{2+}$  ions, reaction (2). In a 1% (v/v) dioxan–water solvent at fixed pH, ionic strength, and total mercury(II) concentration, the addition of chloride, bromide, or thiocyanate ions (as the sodium or potassium salts) leads to a sharp increase in promoting power at concentrations which correspond to those expected<sup>2</sup> to provide the maximum concentration of  $\text{HgX}_2$  species (Figure 1). The effects are not very dependent on the nature of  $\text{X}^-$ . It is clear then that for certain reactions involving neutral substrates neutral mercury(II) species can be better promoters than  $\text{Hg}^{2+}$  itself. This surprising fact is relevant to the reagents used by synthetic chemists to cleave *S*-compounds<sup>3</sup>

For reaction (2) we have also found (by controlling the pH) that the species<sup>2</sup>  $[\text{Hg}(\text{H}_2\text{O})_{x-1}(\text{OH})]^+$  is much more effective in promotion than is  $[\text{Hg}(\text{H}_2\text{O})_x]^{2+}$ . We attribute this to an intramolecular mechanism for the promotion, with (A) and (B) as the respective transition states for the slow step. On this basis the effects of added anions are intelligible: at fixed pH the addition of  $\text{X}^-$  ions to  $\text{Hg}^{2+}$  will reduce its acidity, but will facilitate the intramolecular transfer of any co-ordinated  $\text{H}_2\text{O}$  or  $\text{OH}^-$  owing to the lower positive charge on mercury. A balance of effects is therefore involved and the maximum promotion at  $\text{HgX}_2$  can result.

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## References

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