The Copper(II)-catalysed Hydrolysis of 8-Hydroxyquinoline Sulphate

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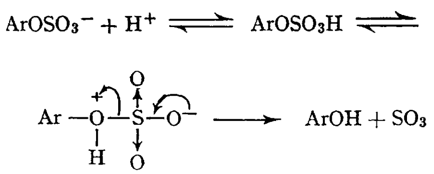
RECENTLY there has been considerable interest in the acid-catalysed hydrolysis of aryl sulphate esters.[1-3] Kice and Anderson have shown[1] that unlike the hydrolysis of the aryl selenates[4] the reaction probably proceeds by an *A*1 mechanism

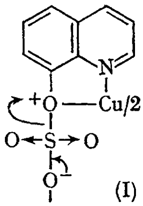


$$ArOSO_3^- + H^+ \rightleftharpoons ArOSO_3H \rightleftharpoons$$

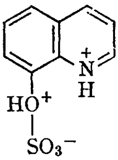
$$Ar-\underset{H}{\overset{+}{O}}-\underset{O}{\overset{O}{S}}-O^- \longrightarrow ArOH + SO_3$$

Nucleophilic catalysis by amines has been observed in the hydrolysis of *p*-nitrophenyl sulphate,[2] and intramolecular carboxyl group catalysis occurs with salicyl sulphate[3] as with salicyl phosphate.[5] We now report that copper(II) ions catalyse the hydrolysis of 8-hydroxyquinoline sulphate.

The reaction was followed spectrophotometrically at 39·8° by monitoring the release of 8-hydroxyquinoline at 253 mμ (λ_{max} for the sulphate ester 240 mμ, λ_{max} 8-hydroxyquinoline 253 mμ in 0·1M-HCl). Excellent pseudo-first-order plots were obtained. For the hydrolysis of 8-hydroxyquinoline sulphate in 3M-HCl the value of k_{obs} is $4·3 \times 10^{-3}$ min.$^{-1}$. In 10^{-3}M-copper(II), with added 0·1 M-KCl to maintain the ionic strength, the value of k_{obs} is $6·25 \times 10^{-3}$ min.$^{-1}$. Separate experiments indicated that potassium chloride did not catalyse the reaction. (The ester concentration was *ca.* 10^{-5}M in the runs.) Hydrolysis is therefore faster in the presence of 10^{-3}M-copper(II) than in 3M-HCl. It is probable that a complex such as (I) is formed, which assists the transfer of electrons from the sulphur–oxygen bond undergoing cleavage. A similar complex has been considered to account for the copper(II)-catalysed hydrolysis of 8-acetoxyquinoline.[6] Formation of the dication (II) from the quinolinium cation would not be expected to be favoured electrostatically; however, hydrolysis of 8-hydroxyquinoline sulphate in 3M-HCl is not greatly slower than that for *p*-nitrophenyl sulphate ($k_{obs} = 7{\cdot}7 \times 10^{-3}$ min.$^{-1}$ in 3M-HCl at 40·2°). Lewis acid-catalysis by copper(II) is probably much more effective than proton catalysis in this case since it does not involve formation of the quinolinium cation. It is noteworthy that most aryl sulphatases have pH-optima in the acidic range (pH 4—6) and although metal ions do not appear to have been implicated in their action,[7] this point has not been definitely established. Detailed kinetic studies of the metal ion-catalysed reactions are in progress.



(I)



(II)

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