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CATALYSIS BY BORIC ACID THROUGH COMPLEX FORMATION

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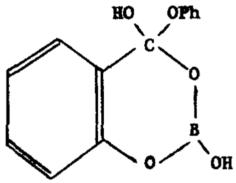
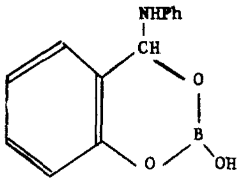
We wish to report that boric acid is an efficient and highly specific catalyst for the hydrolysis of phenyl salicylate and salicylidene aniline. Thus, at 59.2° and pH 8.40 ($\mu = 0.05\underline{M}$) the catalytic constant for buffer catalysis of the hydrolysis of phenyl salicylate in a borate buffer is one hundred times greater than that for the hydrolysis of phenyl o-methoxybenzoate. The imidazole-catalysed hydrolysis of phenyl o-methoxybenzoate, however, proceeds slightly faster than that of phenyl salicylate. In the pH-range 9.5-8.0 the catalytic constant for the hydrolysis of phenyl salicylate in borate buffers increases with decreasing pH, suggesting that boric acid is the catalytically active species, while below pH 8 the constant falls again. A detailed analysis of the pH-rate profile, however, is difficult, owing to the large number of ionisable species present and the similarity of their pK_a's. The magnitude of the boric acid catalysis may be judged by comparing the catalytic constant at pH 8.56 and 59.2°, 3.9×10^{-1} $l.mole^{-1}$ $sec.^{-1}$, with that for catalysis by imidazole, generally considered[1] a good catalyst for ester hydrolysis, which is 4.2×10^{-3} at pH 8.61. Buffer catalysis was not detected in the hydrolysis of p-nitrophenyl acetate in $0.025-0.05\underline{M}$ borate buffers at pH 9.16 and 25°. It is suggested that the boric acid acts by stabilising the tetrahedral intermediate and the transition state for its formation by forming a complex (I). It is clear that the stereochemistry of this ester is suitable for the formation of such a complex, since it is well



(I)



(II)

known[2] that salicylic acid itself forms a borate complex. The hydrolysis of phenyl 5-nitrosalicylate is not catalysed by boric acid, presumably because of the reduced nucleophilicity of the phenolic group. The hydrolysis of catechol monobenzoate, a reaction which involves intramolecular participation by the phenolic group,[3] also does not show boric acid catalysis; with this ester a complex with boric acid analogous to (I) would have a seven-membered ring and its formation would not therefore be favoured.

The effectiveness of this catalysis led us to consider whether it could operate in reactions other than ester hydrolysis and we therefore investigated the hydrolysis of salicylidene aniline. At pH 8.04 the catalytic constant for the hydrolysis in a phosphate buffer of *o*-methoxybenzylidene aniline is twice as great as that for salicylidene aniline, but in a borate buffer it is twenty times smaller. Again the catalytic constant increases with decreasing pH, suggesting that boric acid is the catalytic species, the hydrolysis possibly passing through an intermediate complex (II).

As well as being of theoretical interest, this highly specific catalysis may be of use synthetically, since it should be possible to remove salicoyl and salicylidene groups selectively by means of a boric-acid catalysed hydrolysis.

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