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NEIGHBOURING HYDROXYL GROUP CATALYSIS IN THE HYDROLYSIS OF CARBONATE ESTERS

J.G. Tillett and D.E. Wiggins

Department of Chemistry, University of Essex, Colchester, Essex.

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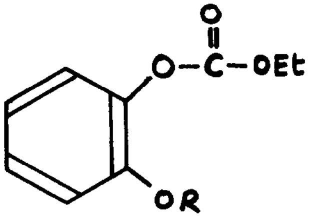
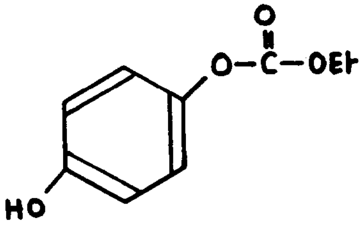
Intramolecular catalysis by a neighbouring hydroxyl group has been reported for the hydrolysis of a number of carboxylic esters and their derivatives (1) - (5) and for phosphate esters (6). We now report the first example of such catalysis in the hydrolysis of carbonate esters.

The pH-rate profile for the hydrolysis of ethyl 2-hydroxyphenyl carbonate Ia, ethyl 2-methoxyphenyl carbonate Ib, and ethyl 4-hydroxyphenyl carbonate II are shown in the Figure.



Ia, R = H

Ib, R = Me



II

At high pH the observed rate of hydrolysis increases rapidly with increase of pH and corresponds to the alkaline hydrolysis of carbonate esters (cf. Ref. 7.). In this region the rates of hydrolysis of all three carbonates studied are very similar. At lower pH's a plateau region is reached which corresponds to a rapid pH-independent neutral or "water" reaction. Comparison of the rates in the latter region shows that carbonate Ia with a neighbouring hydroxyl group undergoes neutral hydrolysis about ten times faster than carbonates Ib or II, suggesting that this group has some direct involvement in the hydrolysis

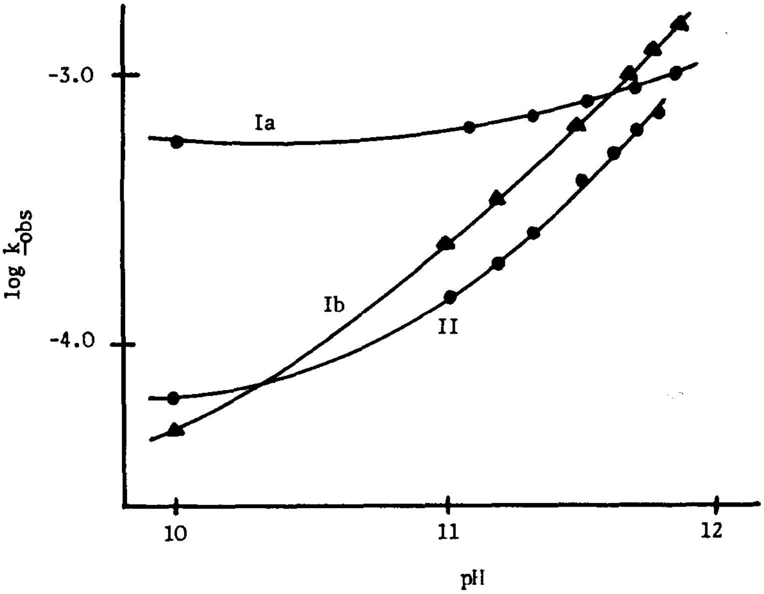
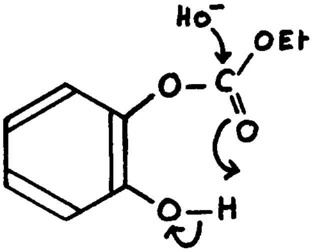


Figure pH-Rate profile for the alkaline hydrolysis of carbonate esters in sodium hydroxide buffers at 25°, ionic strength maintained at 1.0 with KCl (8).

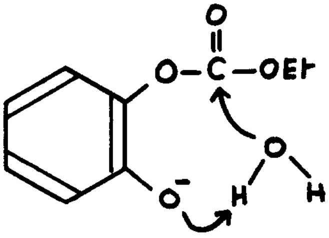
reaction. There are three possible mechanisms which could explain the enhanced rate of hydrolysis of ethyl 2-hydroxyphenyl carbonate, Ia, in the pH-independent region: (i) intramolecular nucleophilic catalysis by the ionized hydroxyl group, (ii) intramolecular general acid catalysis of the attack of hydroxide ion and (iii) intramolecular general base catalysis of the attack of a water molecule.

The first possibility involving rate-determining attack by the ionised hydroxyl group on the carbonyl carbon and formation of a tetrahedral intermediate can be ruled out by consideration of the Arrhenius parameters. The entropy of activation for the neutral hydrolysis of Ia is -41.0 e.u. which is clearly not in the region expected for a unimolecular reaction (9). It is similar in magnitude, however, to the values observed for the neutral hydrolyses of other acyl compounds in water e.g. alkyl trifluoroacetates (10) (-50 e.u.) and acetic anhydride (11) (-40 e.u.). Such values have been attributed to the necessity for the proper orientation of several solvent molecules in the transition state.

The mechanism of intramolecular catalysis in the hydrolysis of Ia must involve therefore one of the two kinetically indistinguishable mechanisms (ii) or (iii) which are outlined in III and IV.



III



IV

If the undissociated hydroxyl group were able to catalyse the attack of hydroxide ion as in III then catalysis with other general bases should be observed. The fact that the addition of sodium acetate (0.500 M) at constant ionic strength has only a small effect on the neutral rate of hydrolysis of ethyl 2-hydroxyphenyl carbonate, k_{H_2O} = 2.04 x 10^{-5} l.mole.$^{-1}$ sec.$^{-1}$ at 35^{o} in the absence of acetate and 2.20 x 10^{-5} l. mole.$^{-1}$ sec.$^{-1}$ in the presence of added acetate, and it has a similar effect on the hydrolysis of ethyl 2-methoxyphenyl carbonate (1.70 and 1.80 x 10^{-6} l. mole.$^{-1}$sec.$^{-1}$ respectively), suggests that general acid catalysis is not involved. Further work is in progress to provide an unequivocal distinction between these two mechanisms.

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8. Kinetics were followed spectrophotometrically at 270 nm for Ia and II and 288 for Ib. Values of the second-order rate-constants for alkaline hydrolysis, k_{OH^-}, were obtained from the slopes of plots of k_{obs} against a_{OH^-}, and values of the pseudo first-order rate constants for the neutral reaction from the intercepts. These were converted to the second-order constant, k_{H_2O}, to represent second-order attack by water. The effect of variation of ionic strength on both k_{OH^-} and k_{H_2O} was found to be small.
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