The Brønsted Acid-catalysed Hydrolysis of Benzoic Anhydride in Aqueous Solutions. Evidence for two Mechanisms and the Effect of Dioxane on their Detectability

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The hydrolysis of benzoic anhydride enjoys two mechanisms of acid catalysis in 60% (v/v) dioxane–water as solvent, one at low and another at high values of $[H_3O^+]$; the former becomes effectively undetectable in a purely aqueous solvent. Implications are discussed.

At 25 °C in 60% (v/v) dioxane–water as solvent, acid catalysis of the hydrolysis of benzoic anhydride is easily detectable at low values of $[H_3O^+]$: the observed first-order rate constant, k_{obs}, increases *ca.* 40-fold between 0 and 3.0 mol dm^{-3} perchloric acid.[1] The details of the acidity and temperature dependences of k_{obs} suggest an A2 mechanism of catalysis.[1] We find that this catalysis is effectively undetectable in purely aqueous solutions of strong acids: with sulfuric acid there occurs an approximately 50% increase in k_{obs} between 0 and 3.0 mol dm^{-3} acid, while with perchloric acid there is a comparable decrease. Such small changes are attributable to salt effects.[2] However, a powerful catalysis is detected at appreciably higher concentrations (Fig. 1). This is very probably of the A1 variety since[3] a plot (Fig. 2) of log k_{obs} − log $[H_3O^+]$ *versus* X (the excess acidity[4]) gives $m^\ddagger > 2$ (based on $m^* \simeq 0.6$ for this O-base[4]) and the plot of log k_{obs} *versus* H_0 has slope 1.0.

Re-examination of the behaviour in 60% dioxane–water over a wider range of acid concentrations than hitherto, supports the previous work, but shows (Fig. 3) that the initial increase in k_{obs} at low values of $[H_3O^+]$ (which is proportional to $[H_3O^+]$) is followed by the type of rapid acceleration found in purely aqueous solutions (and that this occurs at a somewhat lower $[H_3O^+]$ value). Our values of k_{obs} and $\Delta S^\ddagger$ (*ca.* −100 J K^{-1} mol^{-1}) when $[H_3O^+]$ < 3.0 mol dm^{-3} are in satisfactory agreement

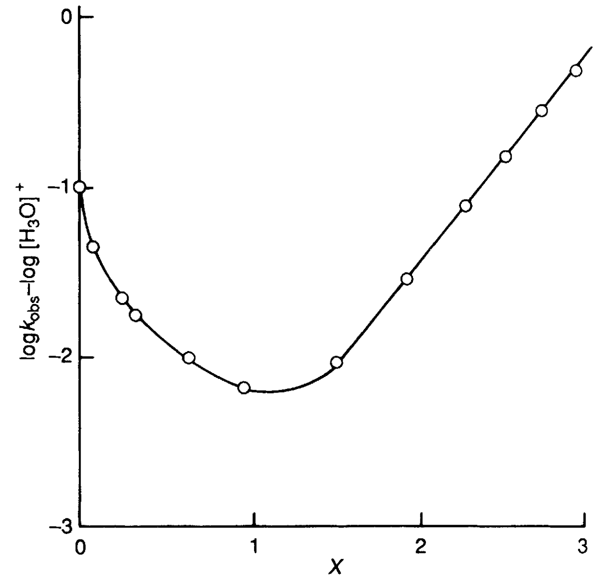

Fig. 2 Plot of log k_{obs} − log $[H_3O^+]$ *versus* excess acidity

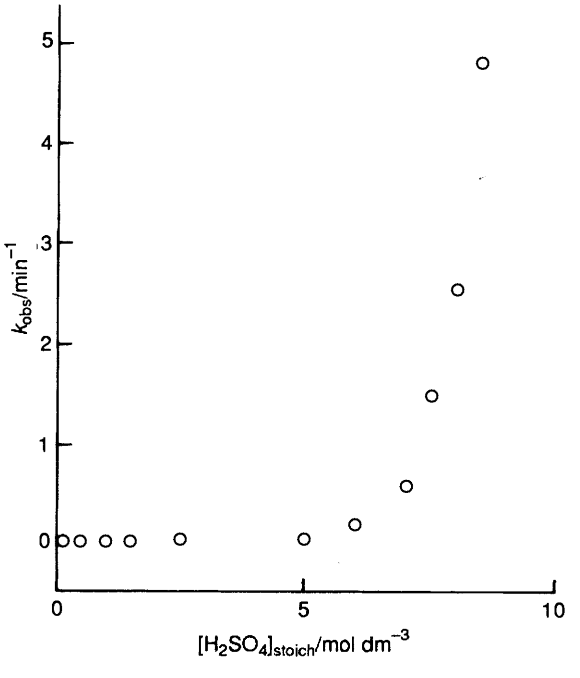

Fig. 1 Hydrolysis of benzoic anhydride in aqueous sulfuric acid at 25 °C. $[\text{Anhydride}]_{initial} = 5 \times 10^{-5}$ mol dm^{-3}.

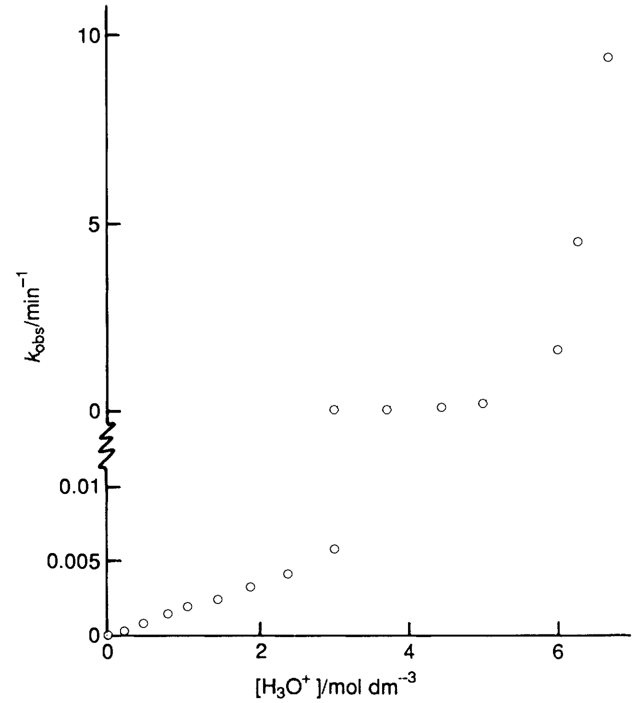

Fig. 3 Hydrolysis of benzoic anhydride in 60% (v/v) dioxane–water mixtures containing perchloric acid at 25 °C. $[\text{Anhydride}]_{initial} =$ 5×10^{-5} mol dm^{-3}.

with the earlier work,[1] and we concur that an A2 mechanism of catalysis is occurring in this region. The sharp change in acidity dependence when $[H_3O^+] \gtrsim 4$ mol dm^{-3} suggests that an A1 mechanism then quickly becomes dominant. When $[H_3O^+] = 6.0$ mol dm^{-3}, $\Delta S^\ddagger \simeq -2$ J K^{-1} mol^{-1}, which is indicative of an A1 mechanism. The suggested change in mechanism is also supported by the behaviour of *p*-toluic anhydride: at 25 °C this anhydride displays a kinetic pattern analogous to that of benzoic anhydride in 60% dioxane–water, but (significantly) leads to similar (or smaller) k_{obs} values when $[H_3O^+] < 2.5$ mol dm^{-3} (A2 region) and (>six-fold) larger values when $[H_3O^+] \simeq 5.0$ mol dm^{-3} (A1 region). Changes in mechanism of acid catalysis with changes in acid concentration have not been found previously for carboxylic anhydrides in any solvent.

In our comparison of solvents, the effect of increasing the water content is greatly to increase the rate of spontaneous hydrolysis (for benzoic anhydride at 25 °C and $[H_3O^+] \simeq 0$, $k_{obs} \simeq 0.3 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} in 60% dioxane–water and 3×10^{-2} dm^3 mol^{-1} s^{-1} in water) but to decrease the relative importance of the catalytic routes, such that the A2 route becomes effectively undetectable in water (30% dioxane shows intermediate behaviour). This result, other recent work of ours with acyl fluorides[5] and aryl isothiocyanates,[6] and certain earlier studies,[2,7] all suggest that the addition to water of increasing amounts of a co-solvent unable to donate protons *via* hydrogen bonds, will increase the importance of acid-catalysed mechanisms of hydrolysis relative to any spontaneous hydrolysis, and sometimes reveal the presence of catalytic mechanisms not evident from the study of purely aqueous solutions. The generality of this result, not obviously predictable, has not been so apparent before.

Studies of changes in acid-catalysed mechanism with changes in solvent acidity have so far been confined largely to aqueous sulfuric acid;[8] we suggest that the use of mixed solvents—often avoided for fear of complications—may provide particularly sensitive media for such studies.

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