The Brønsted Acid-catalysed Hydrolysis of Acyl Fluorides in Aqueous Media; Evidence for Two Mechanisms

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In dioxane–water mixtures rich in dioxane the hydrolysis of benzoyl fluoride is shown to exhibit two mechanisms of acid catalysis: one at low, and one at high values of [H_3O^+]; only the second mechanism (A1) is detectable in pure water.

Of acyl halides only the fluorides have as yet been found to exhibit a Brønsted acid-catalysed hydrolysis in aqueous media. This has been attributed to the greater affinity of F, compared with Cl, Br and I, for protons.[1] In 60:40 (v/v) dioxane–water acetyl and benzoyl fluorides show similar sensitivities to such catalysis compared to their spontaneous rates of hydrolysis.[2] For both, the catalysed path is dependent on [H_3O^+] rather than on h_0, and has been suggested to be an A2-like scheme with protonation on F. For both compounds $k_{H^+}/k_0 \simeq 5$ dm^3 mol^{-1} at 25 °C, where k_{H^+} and k_0 are the catalytic and spontaneous rate constants, respectively. The catalysis is easily detectable when [H_3O^+] $\gtrsim$ 0.1 mol dm^{-3}; it does not arise from a positive salt effect.[3,4] In purely aqueous solutions the spontaneous rate is much greater than in 60:40 dioxane–water, and has increased by roughly the same factor for both fluorides.[3,5,6] For acetyl fluoride an acid-catalysed path is still evident; it is now relatively much more important, with $k_{H^+}/k_0 \simeq 200$ dm^3 mol^{-1} at 0.4 °C, and is detectable when [H_3O^+] $\gtrsim 10^{-3}$ mol dm^{-3}.

In the light of this earlier work, the recent report[6] that benzoyl fluoride shows no acid catalysis at all in water even at [H_3O^+] = 1.0 mol dm^{-3}, is surprising, although a previous study of the hydrolysis of benzoyl fluoride using acetone–water mixtures does suggest that the relative importance of its catalysed path decreases as the water content rises.[3] This contrasting behaviour of the two fluorides does not appear to have been commented on; if correct it has mechanistic implications. Using perchloric acid as the source of hydrogen ions and monitoring the reaction by UV spectroscopy, we have now confirmed the previous work with benzoyl fluoride and have discovered that this fluoride exhibits at least two mechanisms of acid catalysis. We find that in dioxane–water mixtures rich in dioxane [60:40, 50:50, 40:60 (v/v)] the catalysis observed at low acid concentrations, which is proportional to [H_3O^+], becomes less dependent on [H_3O^+] at higher concentrations, and even decreases, until eventually being replaced by a catalysis that increases more rapidly than [H_3O^+]. Fig. 1 shows this effect for a 50:50 (v/v) mixture. Similar behaviour is found in a 60:40 mixture, but the importance of the catalysis at low values of [H_3O^+] declines progressively as the water content of the solvent rises until, in a 20:80 mixture (Fig. 2) only the catalysis at high values of [H_3O^+] remains detectable; the other catalysis has now been swamped by the greater increase in the spontaneous rate. This increase also affects the detectability of the second catalysis which tends to appear at higher acid concentrations as the water content rises. In pure water the behaviour is similar to that shown for the 20:80 mixture.

In media where both the low acid and high acid regions of catalysis are detectable (*e.g.* in a 50:50 mixture) $\Delta H^\ddagger = 76 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -60 \pm 5$ J K^{-1} mol^{-1} for the first region and $\Delta H^\ddagger = 100 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = 20 \pm 4$ J K^{-1} mol^{-1} for the second. For the catalysis in water a plot of log (k_{obs} − k_0) against H_0 is rectilinear with a slope *ca.* 1.0 at 25 °C. *p*-Substituted benzoyl fluorides show analogous behaviour and for the concentrated acid region the catalytic constants corre-

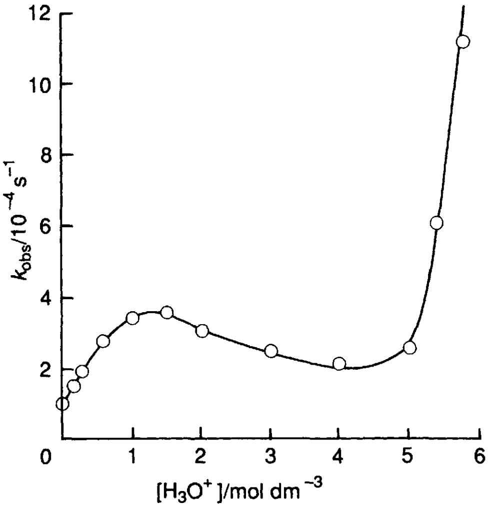

Fig. 1 Hydrolysis of benzoyl fluoride in 50:50 (v/v) dioxane–water at 25 °C. k_{obs} = observed first-order rate constant

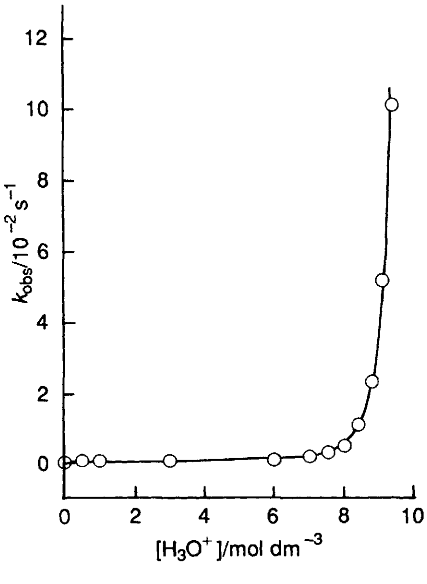

Fig. 2 Hydrolysis of benzoyl fluoride in 20:80 (v/v) dioxane–water at 25 °C

late better with σ^+ than with σ, and $\rho \simeq -6$. Taken together the results suggest an A1 mechanism in strong acid.

The pattern of results obtained now with benzoyl fluoride is somewhat reminiscent of those found for the acid-catalysed hydrolyses of certain esters[7] and amides[8] where A1 mechanisms can take over from A2, or other catalytic mechanisms; it has not been found previously for such reactive carboxylic acid derivatives as acyl fluorides (or anhydrides). The fact that the catalysis found at low acid concentration in the solvent mixture dies out at relatively low values of $[H_3O^+]$ suggests to us that, rather than being an A2 mechanism, it may arise from a mechanism analogous to that thought to apply for esters carrying electron-withdrawing substituents[9,10] ($AB_{Ac}3$ mechanism). Benzoyl fluoride is structurally not unlike a negatively substituted ester. The behaviour of benzoyl fluoride raises questions about the interpretation of the results for acetyl fluoride,[2,5] and suggests that carboxylic anhydrides will also be found to exhibit two mechanisms of catalysis.

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