The Kinetics of Hydrolysis of 4-Ethoxy-2,6-dimethylpyrylium Tetrafluoroborate

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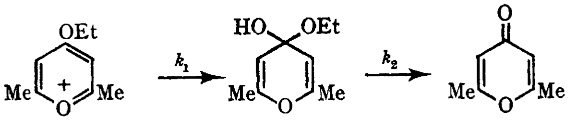
WE report the first kinetic study of the hydrolysis of a 4-ethoxypyrylium salt and the observation of a novel and unexpected pH rate-dependency.

The hydrolysis of the tetrafluoroborate of the 4-ethoxy-2,6-dimethylpyrylium ion (I)[1] was measured over the pH-range 3—9·5. The mechanism of the reaction divided into two steps (k_1 and k_2) characterised by the observation of three u.v. spectra due to reactant (λ_{max} 248 mμ; ϵ, 16,700), intermediate (λ_{max} 255 mμ; ϵ, 14,150), and product (λ_{max} 250 mμ; ϵ, 15,150). The product of hydrolysis in the above pH-range was 2,6-dimethyl-4-pyrone (III) and the stoicheiometry [using the known u.v. absorption of (III)] indicated the absence of competing reactions. At higher pH-values the reaction was not a simple hydrolysis. k_1 was determined by following the change of absorbance at 255 mμ [the isosbestic point between intermediate and (III)]; k_2 was measured at the isosbestic point between intermediate and pyrylium salt (267 mμ), but below pH 4·5 $k_1 < k_2$ and the rate constant is equivalent to k_1.

The hydrolysis product suggests bimolecular attack of oxygen on the ethyl group (S_N2) or addition of water followed by elimination of ethanol as possible mechanisms. The former mechanism is unlikely by analogy with other systems,[2,3] and would not explain the occurrence of an intermediate species. No n.m.r. absorptions other than those expected for pyrylium salt and 4-pyrone were observed during the reaction which is in accordance with the addition mechanism, since the n.m.r. spectrum of the intermediate (II) should be similar to a mixture of ethanol and 4-pyrone. The intermediate is probably not a charge-transfer complex because its rate of formation is relatively slow compared with that for known cases.[4]



(I) (II) (III)

(IV) (V)

Above pH 4·5 it is possible to measure k_2 unequivocally and the reaction is specific acid catalysed. k_1 should follow the rate law $k_1 = k_0 + k_{OH}[OH^-]$ because there are no acids present which ionise in the pH-range studied.

We have observed a novel and unexpected pH-dependency (see Figure) for k_1 which fits the equation

$$k_1 = k_0 + k'/(1 + [H^+]/K_a) + k_{OH}[OH^-]$$

The observed ionisation (K_a) is not due to carbon-bound protons because none of these are exchanged for deuterium at any stage during the reaction in deuterium oxide. The possibility of a buffer effect (k_1 is general base-catalysed) is eliminated because the rate constants are those extrapolated to zero buffer concentration. The hydroxyl of the addition intermediate could ionise in the pH-range studied but this would only affect k_2.

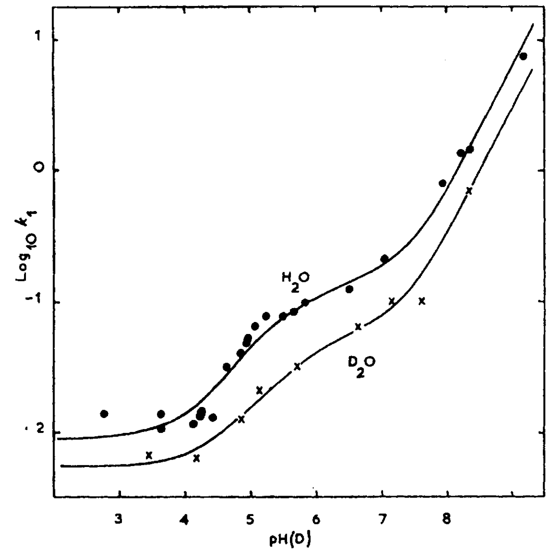


FIGURE. *Lines are derived from the theoretical equation.*

We suggest that K_a arises from the ionisation of the charge-transfer complex (IV) formed between water and the pyrylium ion. The neutral complex (V) then decomposes to give the intermediate (II). The high dissociation constant (K_a) for the proton of the bound water can be explained by the attraction of electrons by the pyrylium nucleus. A simple analogue is the lowering of the pK_a of water from 14 to $-1{\cdot}7$ by its conjugation with a proton.

The proposed mechanism is not capable of direct proof at this time but evidence from the literature[4-6] supports the formation of a charge-transfer complex during similar reactions. The deuterium oxide solvent-isotope effects on the kinetic parameters are in agreement with those expected for the postulated mechanism. K_a

TABLE

	$k_0 \times 10^2$	$k' \times 10^2$	$K_a \times 10^6$	$k_{OH} \times 10^{-5}$
H_2O	0·9 ± 0·05	11 ± 1	4·5 ± 0·5	1·1 ± 0·05
D_2O	0·55 ± 0·05	4·4 ± 0·4	2·7 ± 0·3	3·6 ± 0·4

Parameters (rate constant, M^{-1} min.$^{-1}$; dissociation constant, M) were determined using a curve-fitting programme and refer to 0·1 M-ionic concentration at 50°; $k_2 = 8{\cdot}0 \times 10^2$ M^{-1} min.$^{-1}$ under the same conditions.

decreases in deuterium oxide as expected for acids;[7] the deuteroxide rate constant which could refer either to direct attack at C_4 or to a mechanism involving a pre-equilibrium formation of a complex exceeds that for hydroxide ion as expected for its higher basicity.

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