Direct Observation of the Reversible Ring Opening of the Hydrolysis of 3-Phenyl-2,4,10-trioxa-adamantane

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Summary The equilibrium between a ring-opened oxocarbonium ion and a cyclic ortho ester is observed with 3-phenyl-2,4,10-trioxa-adamantane in sulphuric acid solutions.

THE hydrolysis of 2,4,10-trioxa-adamantanes is known to proceed at a considerably slower rate than that of analogous acyclic ortho esters.[1–3] Consideration of the effect of substituent variation at the 3 position and of the activation entropies has led[2,3] to the suggestion that the rate-determining step is the addition of water to the intermediate oxocarbonium ion, with this species forming reversibly from the ortho ester. We report here the observation of this initial equilibrium, in the case of the 3-phenyl derivative (**1**), and the direct measurement of the rate of hydrolysis of the intermediate ion.

Addition of the ortho ester to sulphuric acid solutions results in the appearance of a new peak in the u.v. spectrum with λ_{max} at 265 nm. This new signal appears very quickly; a stopped-flow experiment in which a neutral aqueous solution of ortho ester was mixed with 30% H_2SO_4 revealed that the signal was present within the dead-time, 2 ms. The signal disappeared much more slowly (Table), at the same rate as the product dihydroxy ester (λ_{max} 232 nm) appeared. The relative intensity of the new peak, extrapolated to zero time, followed a sigmoidal curve (Table), typical of an acid with pK_a = −1·5 (following 1·2 times the H_0 acidity function).

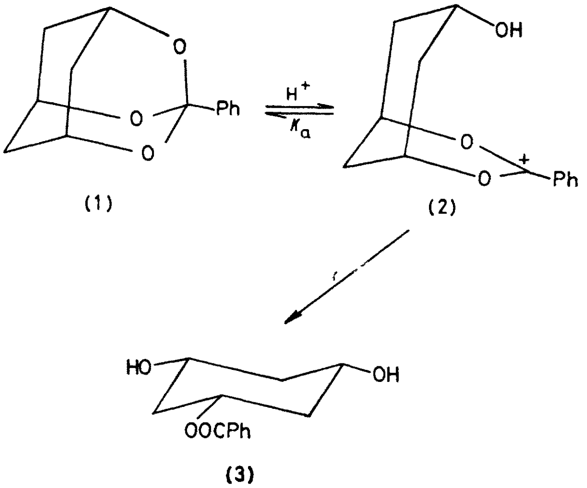
TABLE. 3-Phenyl-2,4,10-trioxa-adamantane in sulphuric acid solutions.

% H_2SO_4	Abs.[a]	10^4 k_{obs}[b]/s^{-1}	10^4 k_{corr}[c]/s^{-1}
0	0·01		
10·5	0·13		
15·5	0·26	15·3	55·0
20·4	0·52	14·2	24·0
24·2	0·62	14·1	21·0
29·7	0·77	5·71	6·6
35·2	0·85	4·50	4·7
41·8	0·87	1·92	1·9
46·0	0·88	0·88	0·88
50·0	0·89	0·45	0·45
56·5	0·89		

[a] Initial absorbance at 265 nm of 6 × 10^{-5} M solutions [b] Rate constant observed for disappearance of the ion (**2**) (at 265 nm) or appearance of product (**3**) (at 232 nm). [c] Rate constant for hydrolysis of ion (**2**), equal to $\{([\mathbf{2}] + [\mathbf{1}])/[\mathbf{2}]\}$-$k_{obs}$.

We propose that this new signal represents the oxocarbonium ion (**2**) forming in these acid solutions in a rapid acid–base type of equilibrium with the ortho ester (**1**) A u v maximum near 265 nm is characteristic of such an ion; other examples include $\mathrm{Ph}\overset{+}{\mathrm{C}}(\mathrm{OMe})_2$[4] and the 2-phenyl-1,3-dioxolan-2-ylium ion [5] We have also obtained an n m r spectrum in concentrated acid, and this too is consistent with the ion structure Proof of the reversibility of the ring opening comes from the finding that neutralization of this solution results only in reformation of ortho ester

One interesting result which comes out of these experiments is the slowness of the further hydrolysis of the ion It is this aspect of the system which allows the initial equilibrium to be observed in the first place Correction of the observed rate constants for ion disappearance for the ortho ester present in the equilibrium (Table), followed by extrapolation to water[6] provides a rate constant in water of $1 \times 10^{-2}\ \mathrm{s}^{-1}$ (It can be noted that in dilute acid where the ion concentration is low, the observed rate constant for the hydrolysis will be given by $k_{\mathrm{H}}[\mathrm{H}^+]$, with $k_{\mathrm{H}} = k/K_{\mathrm{a}} = 3 \times 10^{-4}$ The value[3] reported in 60:40 dioxan–water is $9\ 4 \times 10^{-5}$) The rate in water is a factor of 10^7 smaller than that obtained for $\mathrm{Ph}\overset{+}{\mathrm{C}}(\mathrm{OMe})_2$[6] and 10^6 smaller than that for the 2-phenyl-1,3-dioxolan-2-ylium ion [5] Reasons why the addition of water to (**2**) might be difficult have previously been given A second factor not considered previously is that the addition of water is reversible, as it is with 2-aryl-1,3-dioxolan-2-ylium ions [5]



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