Effect of Acid Concentration on the Hydrolysis of Aziridinium Ions

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Summary The hydrolysis of aziridinium ions is shown, by application of a previously developed solvation approach, to be first order in water molecules.

The marked accelerating effect of acid media on reaction rates has been the subject of many discussions for some time.[1,2] Recently, Bunnett and his co-workers[3] demonstrated that it is possible to separate the effect of the acid medium on the catalytic step of a reaction from its effect on protonation, by selecting a substrate which is already protonated over the acid concentration range of interest. They have shown that the rate of hydrolysis of the aziridinium ion gives a satisfactory correlation with the ($H_0 + \log H^+$) function, as proposed by Bunnett and Olsen.[4] Here we show that an even better correlation can be obtained using an approach which avoids empirical acidity scales and which has a straightforward kinetic interpretation.

In previous publications[5–7] we have shown that the rates of many acid (and base) catalysed reactions are connected with the water content of the medium by the simple

$$k = k_0 \mathrm{H}^+ C_\mathrm{W}{}^n \text{ or } \log(k/H^+) = \log k_0 + n\log C_\mathrm{W} \qquad (1)$$

equation (1).[5] C_W is the molar or volume concentration of water not bound to the proton or to any other major solution component (OH^- in alkali[7]); n can be interpreted as being the order in water of the reaction. This order is generally negative, because the proton, assumed to be primarily tetrahydrated in the 1—10 M range, loses up to 4 water molecules in protonation equilibria. This loss of water will not contribute to n when the substrate is already protonated. Equation (1) then takes the even simpler form of equation (2).

$$k = k_0 C_\mathrm{W}{}^n \text{ or } \log k = \log k_0 + n\log C_\mathrm{W} \qquad (2)$$

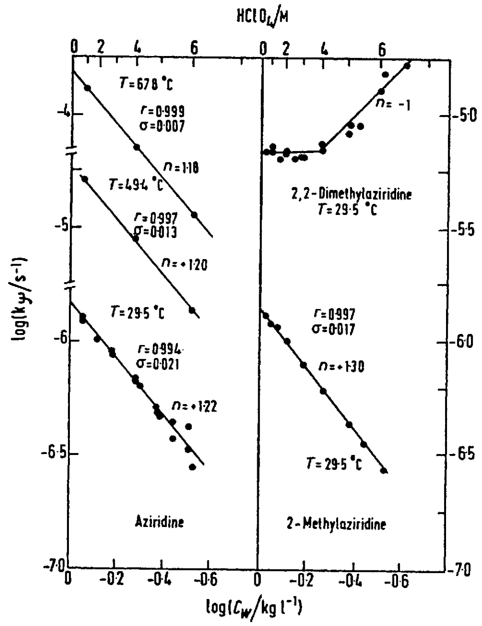

Figure. The hydrolysis of aziridinium ions. The data of Bunnett *et al.* (ref. 3) are plotted according to equation (2). Aziridine: data of Table I in ref. 3; 2-methylaziridine: data of Table II in ref. 3; 2,2-dimethylaziridine: data of Table III in ref. 3; all in $\mathrm{HClO_4}$. LogC_W values are interpolated from Table I of ref. 5. These C_W values are obtained from density data by subtraction of 4 mol of water per 1 mol of acid. The interpolation formula $C_\mathrm{W} = 1 - 0{\cdot}1165\, C_{\mathrm{H}^+}$ can be used. The use of V_W (volume fraction) leads to practically the same results.

In the Figure, the data of Bunnett *et al.*[3] are replotted according to equation (2). Good linear plots are obtained, with correlation coefficients even closer to unity than those reported originally. The slopes for the unsubstituted aziridinium ion as well as those for 2-methylaziridinium ion are not far from unity, indicating a simple first order reaction in water. Slopes of 1·76 and 1·02 were obtained when the data for the hydrolysis of the methylaziridinium ion giving 2-aminopropan-1-ol or 1-aminopropan-2-ol were plotted separately, so that the departure from unity might be due to a different involvement of water in the minor reaction. This departure might, however, also be due to the complete neglect of other medium effects in equation (2).

The closeness of the observed slopes to unity can be interpreted as meaning that aziridinium ion hydrolysis is first order in water. This is in agreement with the S_N2 character ascribed to this reaction,[8] with a single water molecule acting as the nucleophile. The faster hydrolysis of the dimethylaziridinium ion has been proposed to go by an S_N1 mechanism, and, indeed, the Figure shows that this reaction is zero order in water up to 4 M perchloric acid. The inverse first order in water at higher acidities may be due to a progressive contribution of a singly desolvated reactant, such as the dimethyl aziridinium ion, which is favoured by steric influence of the two methyls.

Equation (1) and the hydration approach underlying it thus enable a simple and plausible interpretation of the effect of the medium on this important reaction. A full discussion of why we believe that complete neglect of all activity coefficients, including that of water, is thermodynamically at least as consistent as the partial neglect in other treatments,[2] has been given in previous publications.[5–7]

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