Tetrahedron Letters No. 9, pp 733 - 734, 1974. Pergamon Press. Printed in Great Britain.

THE EFFECT OF WATER STRUCTURE ON THE GENERAL BASE CATALYZED HYDROLYSIS OF COVALENT SULFONYLMETHYLPERCHLORATES

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(Received in UK 21 November 1973; accepted for publication 21 January 1974)

Recently, we reported a kinetic study of the general base catalyzed solvolysis of two arylsulfonylmethylperchlorates in pure water and in water perturbed by the presence of organic solvents or salts.[1]

$$\underset{\underline{1}}{RSO_2CH_2OClO_3} \xrightarrow[-H^{\ominus};\ \text{slow}]{H_2O} RSO_2\overset{\ominus}{C}HOClO_3 \xrightarrow[\text{fast}]{H_2O} RSO_2H + HCOOH + ClO_3^{\ominus}$$

Structure breaking salts were found to decrease the rates of deprotonation (by water as the base) while structure making salts and organic solvents (dioxane or alcohols in low concentrations) induced rate accelerations. The results could be rationalized[1,2] by assuming that the dynamic basicity of water is enhanced when the (diffusionally averaged) water structure[3] is strengthened. We pointed out that the kinetic consequences of varying water structure are very difficult to separate quantitatively from other factors introduced by the presence of the additives (for example, solvent polarity and general base catalysis by sufficiently basic anions or organic cosolvents). Therefore, we did not attempt such a separation and only noticed the consistent trends in the observed solvent and salt effects as support for our hypothesis. These studies have recently been criticized by Pink[4], who, based on a semi-quantitative analysis of the rate accelerations found for $\underline{1}$ (R = $\underline{p}$-$CH_3C_6H_4$) in aqueous solutions of NaF, concluded that "there is no evidence for any effect of water structure on the rates of deprotonation". Assuming that a reliable value for $k_{F^{\ominus}}$ could be obtained from the Brønsted relation derived for a series of carboxylate anions, Pink calculated the fraction of the rate acceleration induced by NaF that cannot be attributed to general base catalysis by $F^{\ominus}$. It was stated[4] that these rate enhancements must be due to hydrolysis by hydroxide ion catalysis, leading to estimates of $k_{OH^{\ominus}}$ between $1.03.10^{6}$ and $1.55.10^{6}$ $l.mole^{-1}.sec^{-1}$ (25^{o}).

We would like to point out that these estimated $k_{OH^{\ominus}}$ values are too high and conflict seriously with experimental evidence. Firstly, the hydrolysis of 1 in pure water obeys pseudo first order kinetics and the rate constant is equal to that in 0.1 N $HClO_4$ within 10%.[1,2] Secondly, in a series of buffer solutions[5] (pH : 3.31 - 4.88) the contribution of the term $(k_{OH^{\ominus}}.c_{OH^{\ominus}} + k_{H_2O}.c_{H_2O})$ to the observed pseudo first order rate constant is constant within experimental error and amounts to $(55 \pm 2).\ 10^{-5}\ sec^{-1}$. Therefore, the upper limit of $k_{OH^{\ominus}}$ is about $2.5.10^{4}$ $l.mole^{-1}.sec^{-1}$. We conclude that the fractional rate enhancements by NaF (as calculated by Pink) cannot be accounted for by assuming hydroxide ion catalysis. Consequently, these rate phenomena should be considered to be the result of salt effects and may, at least partially, arise from the structure making effect of NaF.[6] Although Pink's calculations[4] thus offer some additional support for our hypothesis, it should be stressed that the experimental data obtained thus far do not allow for any reliable quantitative analysis of the influence of water structure on the rates of hydrolysis of covalent sulfonylmethylperchlorates. The obvious complexity of the salt effects on the solvolysis of 1 (because of their dependence on several solvent properties) is clearly illustrated by the following examples: (i) In aqueous dioxane (mole fraction of water: 0.30) of low dielectric constant ($\epsilon = 5.5$ at 25^{o}) and highly ruptured water structure, the structure-breaking LiCl (0.05 N) induced a 23% rate enhancement.[7] This result may be contrasted with the small rate decrease in 0.05 N aqueous LiCl.[1,2] (ii) In anhydrous ethanol, that contains no large three-dimensional hydrogen bond networks, both $(CH_3)_4NCl$ (0.1 N) and LiCl (0.5 N) induce an increase in the rate of solvolysis of 1 (108% and 120%, respectively[7]). In water however, the presence of the structure making $(CH_3)_4NCl$ leads to rate accelerations[1] while the structure-breaking LiCl causes decreased rates of deprotonation.[1]

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