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EFFECT OF WATER STRUCTURE ON PROTON TRANSFER REACTIONS. PART 1.

THE SOLVOLYSIS OF COVALENT SULFONYLMETHYLPERCHLORATES.

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Solvent effects on reaction rates have been accounted for largely in terms of dielectric constants and of solvation.[1] However, in (mixed) aqueous solutions the influence of water structure has also been recognized, most significantly in the case of enzymatic processes.[2] The quantitative evaluation of the importance of these effects is difficult. In simpler systems, the effect of water structure on reaction rates has been considered only occasionally[3-5] and the interpretation of the data is still a matter of controversy.

In an attempt to probe into the question of the effect of water structure on proton transfer reactions, we have measured the rates of hydrolysis of the covalent perchlorates[6] $RSO_2CH_2OClO_3$ (Ia, R = p-$CH_3C_6H_4$; Ib, R = p-$NO_2C_6H_4$) in water in the presence of addenda which are believed to be either "structure-making" or "structure-breaking".

Recent studies[6] have demonstrated that the hydrolysis of Ia and Ib is a kinetically general-base catalyzed reaction involving rate determining proton transfer to a Brønsted base followed by (or concomitant with) rapid product determining steps to give the parent sulfinic acid, formic acid and chloric acid.

$$RSO_2CH_2OClO_3 \xrightarrow[-H^{\oplus}]{H_2O} \left[RSO_2\overset{\ominus}{C}HOClO_3 \right] \xrightarrow{H_2O} RSO_2H + HCOOH + HClO_3$$

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In water there is an easily measured reaction in which only the solvent is acting as a Brønsted base since the pseudo first order rate constants for hydrolysis $k_\psi = k_{H_2O} \cdot c_{H_2O}$ are equal within 10% in pure water and in 0.1N $HClO_4$. Therefore, in the absence of added base, the rates in aqueous solutions are indicative for the propensity of the water molecules to induce an irreversible proton transfer reaction from the substrate. We assume that this propensity is a complex function of solvent properties, including water structure. Since there is abundant evidence[7] that the addition of organic solvents (containing apolar groups) to water has an initial "structure-making" effect on water, we have measured the rates of solvolysis of Ia in H_2O-C_2H_5OH and H_2O-dioxane and Ib in H_2O-C_2H_5OH at 25.00°. Fig. 1 shows a plot of the logarithm of the relative rates of deprotonation vs. mole fraction n_{H_2O} of water. In both solvent systems a rate maximum is observed[*], the initial addition of organic solvent causing an increase in the rate of deprotonation. Especially upon addition of dioxane, a decrease in rate was expected because this solvent of low basicity and dielectric constant will stabilize the ground state and destabilize the transition state. Apparently, these effects only predominate at lower water concentrations. We suggest that the initial rate acceleration is due to the "structure-making" effect of the organic solvent which will facilitate proton transfer to water.[8] It is known that cluster formation provides improved pathways for proton exchange.[7] At 39.80° in H_2O-C_2H_5OH

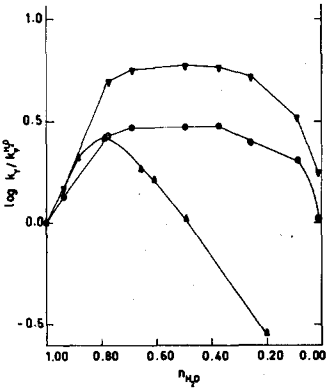

Fig. 1. Relative rates of solvolysis vs. mole fraction of water:
Ia in H_2O-C_2H_5OH, ⊖; Ib in H_2O-C_2H_5OH, ▽;
Ia in H_2O-dioxane, △, (25°).

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[*] Several properties of mixed aqueous solvents have been found to go through maxima, cf. ref. 9.

a rate maximum is still observed for Ia, but the relative differences in k_ψ between $n_{H_2O} = 1$ and $n_{H_2O} = 0.5$ have decreased (i.e. at $n_{H_2O} = 0.496$: $\log k_\psi/k_\psi^{H_2O} = 0.46$ (25.00°) and 0.38 (39.80°)). The data in the Table illustrate that changes in solvent composition cause mutually compensatory changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as has also been observed for some enzymatic reactions.[2]

Table. Activation parameters, kinetic isotope effects ($\frac{k_H}{k_D}$), and solvent deuterium isotope effects ($\frac{k_{ROH}}{k_{ROD}}$) for the solvolysis of Ia and Ib in different solvents.

Substrate	Solvent	$\Delta G^\ddagger$ kcal/mole	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ e.u.	k_H/k_D	k_{ROH}/k_{ROD}
Ia	H_2O	24.4	22.3	-7	6.2	1.68
Ia	H_2O-C_2H_5OH; $n_{H_2O} = 0.496$	22.6	16.6	-20		
Ia	C_2H_5OH	22.8	16.8	-20	6.6	1.82
Ia	H_2O-dioxane; $n_{H_2O} = 0.790$	23.1	13.5	-32		
Ib	H_2O	23.1	18.6	-15		
Ib	H_2O-C_2H_5OH; $n_{H_2O} = 0.496$	21.3	13.8	-25		
Ib	C_2H_5OH	21.4	15.4	-20		

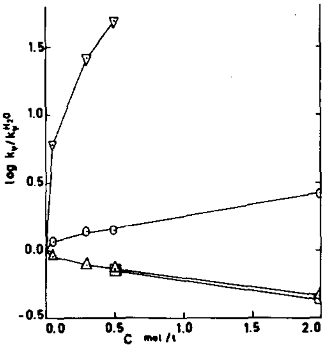

Fig. 2. Rates of hydrolysis of Ia vs. concentration of addendum: ▽ = NaF, ⊖ = $(CH_3)_4N^{\oplus}Cl^{\ominus}$, △ = $NaClO_4$, ⊡ = NaBr.

Cluster formation tends to decrease $\Delta H^{\ddagger}$ whereas $\Delta S^{\ddagger}$ becomes more negative since more "structured" water molecules are involved in the proton transfer reaction.

In accordance with our conclusions, addition of the "structure-making" $(CH_3)_4N^{\oplus}Cl^{\ominus}$ and especially NaF causes rate enhancements while $NaClO_4$ and NaBr, which are "structure-breaking" compounds, lower the rates of hydrolysis (relative rates are plotted in Fig. 2).[10]

Further work on these and other systems is in progress.

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