WATER STRUCTURE OR BASE CATALYSIS? COMMENTS ON THE HYDROLYSIS OF SULFONYLMETHYLPERCHLORATES.

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In their recent paper, EFFECT OF WATER STRUCTURE ON PROTON TRANSFER REACTIONS, Menninga and Engberts[1] attribute the enhanced rate of hydrolysis of sulfonylmethylperchlorates in the presence of NaF to the "water-structure-making" effect of the F^- ion. The rate acceleration due to NaF is marked indeed, especially when compared to the effect of other salts (see Figure).

Although the F^- ion is believed to promote structure making, previous findings[2] do not predict such a singular behaviour. A closer examination of the data[1] suggests that the basicity of F^- accounts for the rate increase so that there is no evidence for any effect of water-structure on the rate - at least not within the concentration range studied.
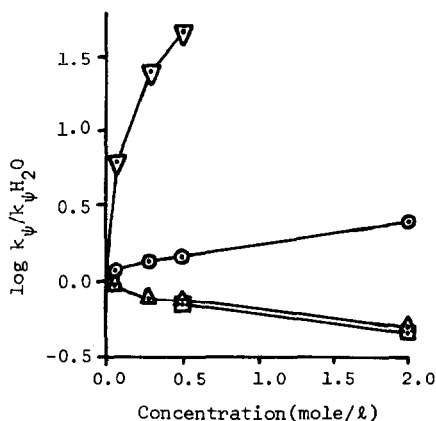

FIGURE. Rates of hydrolysis of $p\text{-}CH_3C_6H_4SO_2CH_2OClO_3$ vs. concentration of addendum (Taken from Reference 1)

▽ NaF

◉ $(CH_3)_4NCl$

△ $NaClO_4$

◻ NaBr

Engberts and coworkers[3] demonstrated that the hydrolysis of sulfonylmethylperchlorates is a general base catalyzed reaction and that nucleophilic displacement can be ruled out. Thus, it is reasonable to assume that the Brønsted relation they found for carboxylic acids should be also valid for HF. From the Brønsted coefficients $\alpha=-2.13$ and $\beta=0.51$ (for $p\text{-}CH_3C_6H_4SO_2CH_2OClO_3$) one

obtains a specific rate constant for the fluoride ion, $k_{F^-} = 0.0305$ ℓ mole^{-1} sec^{-1}.

The F^- ion is a sufficiently strong base so that its hydrolysis is not completely suppressed in the reaction medium, 0.001N HClO$_4$. Although the authors[3] did not report the value of k_{OH^-}, they pointed out that above pH 6 the rate becomes too fast to measure conveniently. The pH of a 0.5M NaF solution is calculated to be 5.85, so the observed rate enhancement is not surprising.

Since the reaction is general base catalyzed, the observed k_ψ is given by: $k_\psi = k_{H_2O}[H_2O] + k_{F^-}[F^-] + k_{OH^-}[OH^-] + k'(F^-)$, where $k'(F^-)$ is the contribution due to solvent structure and depends upon $[F^-]$. The partition of k_ψ, obtained from the Figure, is presented in the Table. The quantity Δ is defined as $\Delta = k_{OH^-}[OH^-] + k'(F^-)$. If $k'(F^-)$ had a significant value, then $\Delta/[OH^-]$ should increase progressively with $[F^-]$. This is obviously not the case and, within experimental error, $\Delta/[OH^-] = k_{OH^-}$ seems reasonable. Thus, at least at low concentration, the effect of NaF does not seem to support the hypothesis of Menninga and Engberts[1].

TABLE. Rate data on the hydrolysis of p-CH$_3$C$_6$H$_4$SO$_2$CH$_2$OClO$_3$, derived from the Figure.

[NaF] (mole/ℓ)	$\log\frac{k_\psi}{k_{H_2O}}$	$k_\psi \times 10^3$ (sec^{-1})	$k_{F^-}[NaF]\times 10^3$ (sec^{-1})	$\Delta\times 10^3$ (sec^{-1})	$[OH^-]$ (mole/ℓ)	$\frac{\Delta}{[OH^-]}\times 10^{-6}$ (ℓ mole^{-1}sec^{-1})
0.	0.	0.54*	–	0.	1×10^{-11}	–
0.05	0.778	3.24	1.50	1.10	7.1×10^{-10}	1.55
0.3	1.417	14.1	9.15	4.41	4.3×10^{-9}	1.03
0.5	1.695	26.8	15.25	11.01	7.1×10^{-9}	1.55

*
From reference 3.

If an ionic type of structure-making addendum is sought, it is suggested that La^{3+} be tried[2]. Other workers[4] found that varying the anions of added salts had a profound effect on the rate of acid catalyzed hydrolysis of esters, but the reaction was insensitive to the nature of the cation. It may be that a base catalyzed reaction would be more influenced by the hydration sphere of a cation.

REFERENCES
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