Hydrolysis of Arylsulfonylmethyl Perchlorates. A Simple Model to Explain Electrolyte Effects on a Water-Catalyzed Deprotonation Reaction

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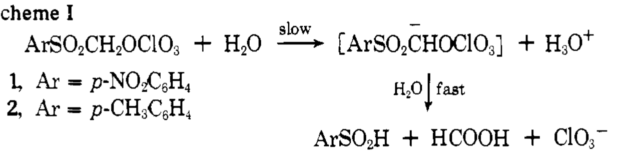
Abstract: In an effort to probe into the effect of electrolytes on the dynamic basicity of water we have studied kinetic salt effects on the water-catalyzed hydrolysis of two covalent arylsulfonylmethyl perchlorates (**1** and **2**). The finding that hydrolysis rates are retarded by cations and enhanced by anions cannot be explained by extended Debye–Hückel or Brönsted theories for molecule–molecule reactions. We propose that the salt effects originate predominantly from electrostatic ion–water interactions and specifically reflect the nature of the dipolar transition state for deprotonation. As demanded by this model, the magnitude of the salt effects is governed by the charge densities of the ions. Effects due to electrolyte-induced changes in the diffusionally averaged water structure are also discussed and are invoked to explain the pronounced $\Delta H^{\ddagger}$-$\Delta S^{\ddagger}$ compensation behavior and the changes in the solvent deuterium isotope effect in aqueous solutions containing varying concentrations of n-$\mathrm{Bu_4NBr}$. Analysis of these effects hinges on the interpretation of the thermodynamics of transfer of two model substrates from water to aqueous salt solutions. Consistent with the advanced interpretation, salt effects on the hydrolysis of **1** in aqueous dioxane and on the ethanolysis of **1** in ethanol differ substantially from those observed in aqueous solutions.

Simple electrostatic theory for aqueous electrolyte solutions (extended Debye-Hückel and Brönsted theories) predicts positive salt effects for molecule–molecule reactions involving charge separation in the transition state.[1-4] In sufficiently dilute solutions these salt effects are expected to be independent of the nature of the electrolyte. Several reactions do not follow these predictions.[5,6] Consequently, specific parameters have been introduced to account for these pecularities and among these, the importance of the charge densities of the ions has especially been emphasized.[5] However, no general and quantitative theory has yet been developed to describe either the thermodynamic parameters for transfer of a nonelectrolyte from water to the aqueous salt solution[7-12] or the change of the activity coefficient as a function of salt concentration. To date, the most successful semiempirical theory is provided by the concept of internal pressure as described by Long and McDevit.[13,14]

In this paper primary kinetic salt effects are reported for the water-catalyzed hydrolysis of covalent arylsulfonylmethyl perchlorates (**1** and **2**), which constitutes an example of a molecule–molecule reaction. Previous kinetic studies have shown that this pH-independent hydrolysis reaction involves rate-determining proton transfer from the substrate to water (Scheme I).[15]

Scheme I



$$\mathrm{ArSO_2CH_2OClO_3} + \mathrm{H_2O} \xrightarrow{\text{slow}} [\mathrm{ArSO_2\overset{-}{C}HOClO_3}] + \mathrm{H_3O^+}$$

1, Ar = p-$\mathrm{NO_2C_6H_4}$

2, Ar = p-$\mathrm{CH_3C_6H_4}$

$$\Big\downarrow{\scriptstyle \mathrm{H_2O}}\ \text{fast}$$

$$\mathrm{ArSO_2H} + \mathrm{HCOOH} + \mathrm{ClO_3^-}$$

Recently, we have employed this reaction as a specific probe for the dynamic basicity of water in mixed aqueous solutions[16-18] and in micellar solutions.[19] We now present a simple model designed to explain the effect of electrolytes on the dynamic basicity of water in aqueous solutions. We feel that an analysis of the salt effects in terms of activity coefficient behavior of ground state and transition state offers no real explanation for the effect of electrolytes on the dynamic basicity of water.[20] Therefore, we have sought for a rationalization mainly emphasizing effects due to (i) electrostatic solvation and (ii) water structure perturbation.[21]

Results

Solvolysis of 1 and 2 in Salt Solutions. Pseudo-first-order rate constants (k_{obsd}), activation parameters, and isotope effects for the hydrolysis of **1** and **1a** (p-$\mathrm{NO_2C_6H_4SO_2CD_2OClO_3}$) in aqueous salt solutions are presented in Table I. The effects of HCl and $\mathrm{HClO_4}$ on the hydrolysis rates are treated as salt effects since the hydrolysis of **1** and **2** is not subject to acid catalysis.[15] For electrolytes containing monovalent ions, plots of log $k_{\mathrm{obsd}}/k^0_{\mathrm{obsd}}$ ($k^0_{\mathrm{obsd}} = k_{\mathrm{obsd}}$ in water in the absence of salt) vs. salt concentration are displayed in Figure 1. Generally, inorganic salts *decrease* the rate of hydrolysis (except CsCl) and tetraalkylammonium halides *increase* the hydrolysis rate. Analogous results are obtained for the hydrolysis of **2** (Table II). As evidenced by the magnitude of the primary kinetic deuterium isotope effect (Table I), the presence of KBr and n-$\mathrm{Bu_4NBr}$ does not affect the mechanistic pathway for hydrolysis. Previously, it has already been shown that even in the presence of strong nucleophiles the mechanism is not changed toward nucleophilic displacement at the α-sulfonyl carbon atom.[15]

Kinetic salt effects on the hydrolysis of **1** in $\mathrm{H_2O}$–dioxane are summarized in Table III. These data pertain to water-catalyzed processes since **1** is stable in pure dioxane.[15,18] Figure 2 shows plots of log $k_{\mathrm{obsd}}/k^0_{\mathrm{obsd}}$ ($k^0_{\mathrm{obsd}} = k_{\mathrm{obsd}}$ in $\mathrm{H_2O}$-dioxane) vs. salt concentration for $\mathrm{H_2O}$–dioxane solutions of $n_{\mathrm{H_2O}} = 0.70$. In striking contrast to the results for the aqueous salt solutions, the inorganic salts now show positive salt effects, the only exceptions being $\mathrm{NaClO_4}$ and $\mathrm{HClO_4}$.

Pseudo-first-order rate constants and activation parameters for ethanolysis[17] of **1** in ethanol containing LiCl and n-$\mathrm{Bu_4NBr}$ are shown in Table IV. In Figure 1 log $k_{\mathrm{obsd}}/k^0_{\mathrm{obsd}}$ ($k^0_{\mathrm{obsd}} = k_{\mathrm{obsd}}$ in pure ethanol) is plotted as a function of salt concentration; the changes of $\Delta H^{\ddagger}$ and $-T\Delta S^{\ddagger}$ upon changing salt concentration are shown graphically in Figure 3. It is important to note that LiCl has a positive salt effect on the ethanolysis in contrast to the rate decrease found for the aqueous LiCl solutions. The effect of n-$\mathrm{Bu_4NBr}$ is rate accelerating in ethanol as well as in water.

Thermodynamic Parameters of Transfer of 3 and 4. In order to gain a better understanding of the electrolyte effects on the enthalpy and entropy of the initial state and the transition state for deprotonation of **1** and **2**, the availability of thermodynamic parameters for transfer of **1** and **2** from water to the aqueous salt solutions would be highly desirable. However, **1** and **2** are too readily hydrolyzed to allow the measurements of these quantities. To solve this unfortunate problem, we chose two model substrates **3** and **4** of related structure and determined

Table I. Pseudo-First-Order Rate Constants (k_{obsd}; 25 °C), Activation Parameters, and Isotope Effects for the Hydrolysis of **1** and **1a** in Aqueous Salt Solutions Containing 10^{-3} M HCl

Compd	Salt[a]	Concn[b]	$10^4 k_{obsd}$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Isotope effect
1			32.5	18.4	−8	
1a			5.82	19.2	−9	5.6[c]
1	HCl	0.50	27.5	18.5	−8	
1	$HClO_4$	0.50	21.5	18.8	−8	
1	LiCl	0.50	29.1	18.4	−8	
1	NaCl	0.50	28.8	18.5	−8	
1	CsCl	0.50	32.7	18.5	−8	
1	NaBr	0.50	29.5			
1	KBr	0.50	29.5	18.3	−9	
1	KBr	1.00	26.3	18.7	−8	
1	KBr	1.50	24.7	18.4	−9	
1a	KBr	0.50	5.11	18.9	−10	5.8[c]
1a	KBr	1.00	4.73	19.1	−10	5.6[c]
1	$NaClO_4$	0.25	28.9	18.3	−9	
1	$NaClO_4$	0.50	25.4	18.3	−9	
1	$NaClO_4$	1.00	20.5	18.8	−8	
1	$MgCl_2$	0.50	24.2			
1	$CaCl_2$	0.50	25.1			
1	Na_2SO_4	0.50	93.1			
1	Me_4NBr	0.20	33.1	18.6	−8	
1	Me_4NBr	0.80	36.3	18.8	−7	
1	n-Bu_4NBr	0.05	36.1	18.5	−8	
1	n-Bu_4NBr	0.10	36.7	18.6	−7	
1	n-Bu_4NBr	0.20	42.9	18.9	−6	
1	n-Bu_4NBr	0.30	53.4	19.1	−5	
1	n-Bu_4NBr	0.50	87.0	19.6	−2	
1	n-Bu_4NBr	0.80	164	20.8	+3	
1a	n-Bu_4NBr	0.30	12.7	19.7	−6	4.2[c]
1a	n-Bu_4NBr	0.80	39.8	21.4	+2	4.1[c]
1	(D_2O)		18.6	18.6	−9	
1	$KBr(D_2O)$	0.50	16.8	18.9	−8	1.8[d]
1	$KBr(D_2O)$	1.00	15.2	19.0	−8	1.7[d]
1	n-$Bu_4NBr(D_2O)$	0.30	37.6	18.9	−6	1.4[d]
1	n-$Bu_4NBr(D_2O)$	0.80	155	21.6	+6	1.1[d]

[a] In H_2O unless otherwise indicated. [b] Concentrations in moles per 55.5 mol of solvent. [c] Primary kinetic deuterium isotope effect. [d] Solvent deuterium isotope effect.

their free enthalpies ($\Delta G_{tr}°$), enthalpies ($\Delta H_{tr}°$), and entropies ($\Delta S_{tr}°$) of transfer employing the solubility method of Jolicoeur and Lacroix.[22] Results are given in Table V and are plotted in Figure 4.

p-$\mathrm{CH_3C_6H_4SO_2CH_2OSO_2C_6H_5}$

3

p-$\mathrm{CH_3C_6H_4SO_2CD_2ONO_2}$

4

Table II. Pseudo-First-Order Rate Constants (k_{obsd}) for the Hydrolysis of **2** in Aqueous Salt Solutions Containing 10^{-3} M HCl (25 °C)

Salt	Concn[a]	$10^4 k_{obsd}$, s^{-1}
		6.05
LiCl	0.50	5.50
NaCl	0.10	5.83
NaCl	1.00	5.25
NaCl	2.00	4.52
NaBr	0.50	4.37
NaBr	2.00	2.64
$NaClO_4$	0.05	5.49
$NaClO_4$	0.30	4.73
$NaClO_4$	0.50	4.48
$NaClO_4$	2.00	2.85
Me_4NCl	0.05	7.08
Me_4NCl	0.30	8.36
Me_4NCl	0.50	8.56
Me_4NCl	2.00	16.1
n-Bu_4NCl	0.200	8.78
n-Bu_4NBr	0.200	9.86
n-Bu_4NBr	0.305	11.51
n-Bu_4NBr	0.800	54.4

[a] Concentrations in moles per 55.5 mol of water.

Discussion

Kinetic Salt Effects in Aqueous Solution. The negative kinetic salt effects on the rates of hydrolysis of **1** and **2** found for the aqueous solutions of inorganic salts (except CsCl; Tables I and II) are unexpected. These results provide another demonstration that the reaction between two neutral reactants leading to charge separation in the transition state is not necessarily accelerated by the presence of electrolytes as demanded by simple electrostatic theory. Since at least one water molecule will be strongly bound in the transition state for deprotonation of **1** and **2** (schematically depicted[23] in structure **5**), it is tempting to explain the salt effects by invoking the operation of water structure effects on the hydrolytic process.[24] It is known that most inorganic salts which possess dominating type II_{sb} cosphere effects[25] disrupt the diffusionally averaged water structure to a significant extent.[21,26] This effect would possibly lead to decreased transition state solvation as compared with that in pure water.[27] At first sight, the *positive* salt effect of the "structure-making" tetraalkylammonium

Table III. Salt Effects on the Hydrolysis of **1** in H_2O-Dioxane Mixtures at 25 °C

Solvent	n_{H_2O}[a]	Salt	Concn[b]	$10^4 k_{obsd}$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$k_{obsd}{}^{c}/k_{obsd}{}^{H_2O}$
H_2O	1.00			32.5	18.4	−8	
H_2O-dioxane	0.90			111	15.6	−15	
H_2O-dioxane	0.90	LiCl	1.00	123	14.1	−20	
H_2O-dioxane	0.70			148	13.0	−23	4.4
H_2O-dioxane	0.70	LiCl	0.50	189	13.3	−22	6.5
H_2O-dioxane	0.70	LiCl	1.00	215			
H_2O-dioxane	0.70	HCl	0.50	184			6.7
H_2O-dioxane	0.70	NaCl	0.50	170			5.9
H_2O-dioxane	0.70	CsCl	0.50	160			4.9
H_2O-dioxane	0.70	NaBr	0.50	161			5.5
H_2O-dioxane	0.70	NaBr	1.00	175			
H_2O-dioxane	0.70	$HClO_4$	0.50	110			5.1
H_2O-dioxane	0.70	$NaClO_4$	0.50	112			4.4
H_2O-dioxane	0.70	n-Bu_4NBr	0.50	422			4.9
H_2O-dioxane	0.50			79.4			
H_2O-dioxane	0.50	LiCl	0.50	112			

[a] Mole fraction of water. [b] Concentrations in moles per 55.5 mol of solvent. [c] $k_{obsd}{}^{H_2O}$ = pseudo-first-order rate constant for hydrolysis in the aqueous salt solution in the absence of dioxane.

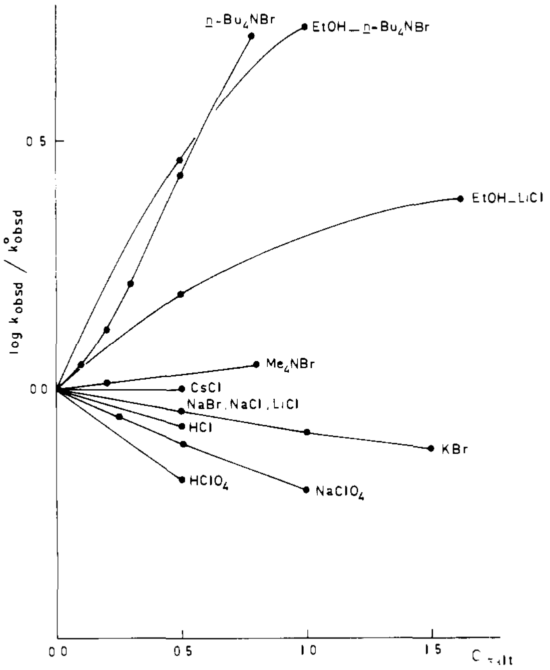
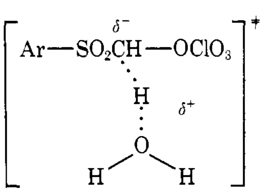


Figure 1. Plots of log k_{obsd}/k^0_{obsd} as a function of salt concentration (aquamolality scale) for hydrolysis of **1** in aqueous electrolyte solutions.



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salts[21,26] (Tables I and II) could then be rationalized on the basis of this concept. However, we find no correlation between the rate decreasing effectiveness of the inorganic salts and the magnitude of their water structure perturbing capacity. The "structure breaking" effect of cations and anions is in increasing order of effectiveness:[21,26] n-$Bu_4N^+ < Mg^{2+} < Ca^{2+} < Me_4N^+ < Li^+ < Na^+ < K^+ < Cs^+$ and $SO_4{}^{2-} < Cl^- < Br^- < ClO_4{}^-$, where n-Bu_4N^+, Mg^{2+}, Ca^{2+}, Me_4N^+, Li^+, and Na^+ are in fact "structure makers". The salt effects on the hydrolysis of **1** follow the sequence $HClO_4 > MgCl_2 > CaCl_2 > NaClO_4 > HCl > NaCl \sim LiCl \sim NaBr \sim KBr > CsCl > Me_4NBr > n$-$Bu_4NBr > Na_2SO_4$ (Table I) and, for the hy-

Table IV. Pseudo-First-Order Rate Constants (k_{obsd}; 25 °C) and Activation Parameters for the Solvolysis of **1** in Ethanolic Salt Solutions

Salt	Concn[a]	$10^4 k_{obsd}$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
		45.1	15.8	−16
LiCl	0.50	69.8	17.1	−11
LiCl	1.62	108	18.8	−5
n-Bu_4NBr	0.50	129	17.0	−10
n-Bu_4NBr	0.65	171	16.9	−10
n-Bu_4NBr	1.00	240	17.1	−9
n-Bu_4NBr	1.13	299	17.0	−9
n-Bu_4NBr	1.94	641	17.1	−7

[a] Concentrations in moles per 55.5 mol of solvent.

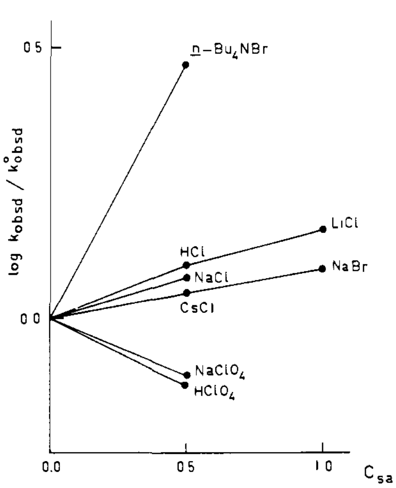

Figure 2. Plots of log k_{obsd}/k^0_{obsd} (see text) as a function of salt concentration (aquamolality scale) for hydrolysis of **1** in H_2O-dioxane, n_{H_2O} = 0.70.

Table V. Thermodynamic Quantities of Transfer from Water to Aqueous Salt Solutions for **3** and **4**

Compd	Solvent	Salt	Concn[a]	$\Delta G_{tr}°$, cal mol^{-1}	$\Delta H_{tr}°$, kcal mol^{-1}	$\Delta S_{tr}°$, eu
3	H_2O	n-Bu_4NBr	0.80	−1960	5.4	25
3	H_2O	n-Bu_4NBr	1.60	−3300	2.0	18
4	D_2O			86	0.2	0
4	H_2O	KBr	0.50	57	−0.6	−2
4	D_2O	KBr	0.50	60	−0.2	−1
4	H_2O	n-Bu_4NBr	0.15	−331	0.2	2
4	H_2O	n-Bu_4NBr	0.30	−533	0.5	3
4	H_2O	n-Bu_4NBr	0.50	−840	1.0	6
4	H_2O	n-Bu_4NBr	0.80	−1280	4.8	20
4	D_2O	n-Bu_4NBr	0.30	−577	0.9	5
4	D_2O	n-Bu_4NBr	0.80	−1210	5.8	24

[a] Salt concentrations in moles per 55.5 mol of solvent.

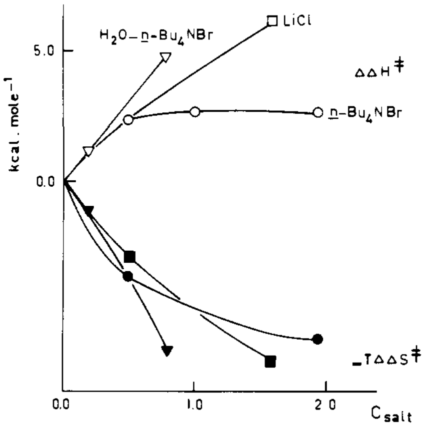

Figure 3. Plots of $\Delta\Delta H^{\ddagger}$ and $-T\Delta\Delta S^{\ddagger}$ as a function of salt concentration for ethanolysis of **1** in ethanol containing LiCl or n-Bu_4NBr and for hydrolysis of **1** in aqueous n-Bu_4NBr.

drolysis of **2**, $NaClO_4 \sim NaBr > NaCl > LiCl > Me_4NCl > n\text{-}Bu_4NBr$ (Table II). If water structure effects or salting-in and salting-out parameters would *dominate* the sign and magnitude of the salt effects, CsCl would cause a stronger rate decrease than LiCl, which is in contradiction with the experiment.

The observed salt effects may be rationalized, however, by assuming that the magnitude of the salt effect is primarily determined by the charge type and charge density[28] of the distinct ions. The salt effects of the single ions on the hydrolysis of **1** and **2** follow the sequences $Mg^{2+} > Ca^{2+} > H^+ > Li^+ \sim Na^+ \sim K^+ > Cs^+ > Me_4N^+ > n\text{-}Bu_4N^+$ and $ClO_4^- > Br^- > Cl^- > SO_4^{2-}$, corresponding with the order of charge densities. Our results suggest, therefore, the existence of an electrostatic interaction between the dipolar transition state and the electrostatic field of the ions operating via polarized water molecules between the ion and the partially broken C–H bond.[29] Of course, the polarization effects as proposed here will be strongly attenuated because those ions which possess small effective ionic radii also have highly developed hydration cospheres which effectively hamper close proximity between the ion and the organic solute.[30] The importance of this leveling effect will be related to the partial molal volumes of the ions.[31] Since solvation of the dispersed negative charge formed at the α-sulfonyl carbon atom in the transition state is relatively unimportant as compared with the solvation of the positive charge[18] (structure **5**), the above theory offers a ready explanation for the negative salt effect of cations and the positive salt effect of anions.[32] A similar theory has been advanced long ago by Olson et al.[6] for salt effects on the hydrolysis of acetals.

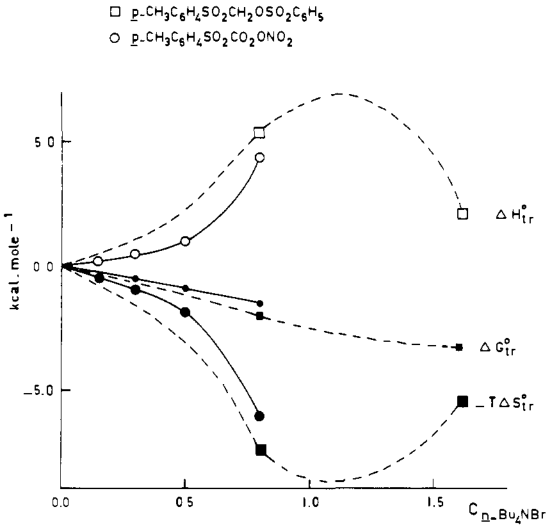

Figure 4. Plots of $\Delta G_{tr}°$, $\Delta H_{tr}°$, and $-T\Delta S_{tr}°$ for transfer of **3** and **4** from water to aqueous solutions of n-Bu_4NBr. The different concentrations of n-Bu_4NBr are expressed in the aquamolality scale.

Usually, however, specific salt effects have been interpreted in terms of direct transition state–ion interaction (especially in nonaqueous solvents)[33] or by considering the decrease in the availability of water molecules as a function of electrolyte concentration. For example, the latter theory has been advanced as a rationale for electrolyte effects on the neutral hydrolysis of acetic anhydride.[5,34] In this case, the rates of hydrolysis are retarded by *both* cations and anions following the sequences $Bu_4N^+ \gg Rb^+ \sim Na^+ \sim Cs^+ > Li^+$ and $I^- > Br^- > Cl^-$. As expected, these sequences also correspond with increasing charge densities. However, the opposite effects of cations and anions on the rate of hydrolysis of **1** and **2** cannot be reconciled with this concept which, consequently, constitutes no comprehensive measure for the dynamic basicity of water in electrolyte solutions. This is also illustrated by the salt effects on the water-induced detritiation of *tert*-butylmalononitrile already referred to above.[20] The transition state for this reaction is essentially an ion pair $RC^- \cdots H_3O^+$ (Brönsted β = 0.98 ± 0.02) but the gross features of the mechanism resemble those for the deprotonation of **1** and **2** (Brönsted $\beta \simeq 0.5$).[15] The rates are increased by tetraalkylammonium halides and decreased by LiCl, NaCl, and KCl. Again, the effects of the individual ions are found to correlate with their effective charge densities: $Li^+ \gtrsim Na^+ \gtrsim K^+ > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$ and $Br^- > Cl^-$.

Water Structure Effects. The effect of changes in the (diffusionally averaged) water structure[21] on relatively slow proton transfer reactions is second-order. It is usually manifested by the occurrence of characteristic and pronounced $\Delta H^{\ddagger}$-$\Delta S^{\ddagger}$ compensation phenomena[27,35,36] when the structural integrity of the highly aqueous medium is varied gradually. This type of behavior may well leave $\Delta G^{\ddagger}$ practically unchanged.[37] On the basis of the following observations we venture to suggest that the hydrolysis of **1** and **2** responds to changes in water structure in electrolyte solutions: (i) the changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as a function of electrolyte concentration are much more pronounced for n-Bu_4NBr than for any other salt we have investigated (Tables I and II) and (ii) the solvent deuterium isotope effect ($k(H_2O)/k(D_2O)$) for **1** decreases from 1.7 in the absence of salt to 1.1 in 0.80 M n-Bu_4NBr. In order to explain both observations, we first turn our attention to the thermodynamic quantities of transfer from water to aqueous n-Bu_4NBr solutions for the model substrates **3** and **4** (Table V). In a good approximation, the enthalpy of transfer ($\Delta H_{tr}°$) of nonelectrolytes may be analyzed in terms of two contributions, both relative to those pertaining to water as the solvent: (a) the enthalpy necessary to create a cavity in the solvent in order to accommodate the solute and (b) the enthalpy of solvation of the solute.[38] For neutral organic molecules, term a is usually the dominant one since solute–water interaction is less favorable in the enthalpic sense than water–water interaction. Taking into account the well-documented water structure promoting effect of n-Bu_4NBr,[39] which is due to the hydrophobic alkyl chains in the cation, the endothermic $\Delta H_{tr}°$ values will primarily reflect the more difficult cavity formation as water structure is enhanced by the presence of n-Bu_4NBr.[40] Consistent with this interpretation, the $\Delta S_{tr}°$ values are positive and, interestingly, they overcompensate the $\Delta H_{tr}°$ terms to make $\Delta G_{tr}°$ exothermic.[41] If one considers the $\Delta H_{tr}°$ values (especially for **4** which is structurally very related to **1** and **2**) in relation to the $\Delta H^{\ddagger}$ values for hydrolysis of **1** and **2** in aqueous n-Bu_4NBr,[42] it may be concluded that the marked increase of $\Delta H^{\ddagger}$ with salt concentration is largely due to transition state effects. Two factors may be responsible for the increase of $\Delta H^{\ddagger}$ in the region 0–1.2 M n-Bu_4NBr. First, cavity formation for the initial state will require less enthalpy than for the more voluminous transition state. However, this effect will be attenuated by the more favorable C–H···OH_2 hydrogen bond interaction for the transition state in more structured water. Second, hydrophobic contacts may occur between the apolar substrate and the n-Bu_4N^+ ion which will discourage deprotonation by water molecules. Again the enthalpy variation is accompanied by mirror image behavior of the entropy, the overall result being a modest decrease of $\Delta G^{\ddagger}$ with increasing concentration of n-Bu_4NBr. Since the positive kinetic salt effect of n-Bu_4NBr appears to arise from entropy rather than enthalpy terms, we can now rationalize the decrease of the solvent deuterium isotope effect in n-Bu_4NBr solutions (vide supra). Previous work has indicated that quite generally water structure perturbation is more manifest in D_2O than in H_2O.[43-45] This will result in more positive $\Delta S^{\ddagger}$ values for hydrolysis in n-Bu_4NBr–D_2O than in n-Bu_4NBr–H_2O of the same salt concentration (in aquamolality units) and, consequently, this will lead to smaller values of $k(H_2O)/k(D_2O)$.

Further support for the present analysis is provided by the observation (Table V) that $\Delta H_{tr}°$ and $\Delta S_{tr}°$ vary in *opposite* direction (as compared with transfer to the n-Bu_4NBr solutions) for transfer of **4** from water to a 0.50 M KBr solution. Since KBr is recognized to be structure breaking, cavity formation in aqueous KBr will require the rupture of less hydrogen bonds relative to pure water.[39] The accompanying negative $\Delta S_{tr}°$ term is responsible for the small and positive $\Delta G_{tr}°$. This leads to the conclusion that the small and negative salt effect of KBr on the hydrolysis of **1** and **2** will find its origin in dominant transition-state solvation effects. It may reasonably be assumed that in aqueous KBr solutions of diminished water structure the propensity for strong CH···OH_2 interaction will be decreased. The rates of hydrolysis of **1** and **2** in mixed aqueous solution also proved to be susceptible to this factor.[17,36] In the aqueous electrolyte solutions these water structure effects will, therefore, tend to modulate the electrostatic effects described in the previous section.

Salt Effects in H_2O–Dioxane and in Ethanol. Since there is compelling evidence that cations are solvated preferentially by dioxane,[46-49] it is expected that the gradual replacement of water by dioxane will cause a decrease of the specific effect of the cations on the hydrolysis rate relative to that of the anions. Salt effects in H_2O–dioxane (Table III) reveal that this expectation is borne out in practice. The most striking result is that now HCl, LiCl, NaCl, and NaBr are rate enhancing in contrast to their negative salt effects in water. As expected, all salt effects are enhanced in H_2O–dioxane relative to water, because of the lower dielectric constant of the medium and the decreased solvation number of the ions.[50] The increase of the salt effect as compared with that in water follows the sequence HCl > LiCl > NaCl > $HClO_4$ > CsCl > n-Bu_4NBr > $NaClO_4$ (hydrolysis of **1** in H_2O–dioxane, $n_{H_2O} = 0.70$). This is in accord with the expected order based on the charge densities of the cations and anions. We now turn to the kinetic salt effects observed in ethanol (Table IV). This is also a less polar solvent than water (ϵ 24.3 vs. 78.4 for water), but now the dynamic basicity of the organic solvent molecules is comparable to that of water. The data in Table IV reveal that, as for H_2O–dioxane, there is a substantial increase of the anion effect relative to the cation effect as demonstrated by the *positive* salt effect of LiCl. Electrostriction of ethanol molecules will be dependent on the charge densities of the ions (LiCl > n-Bu_4NBr) and will be the major factor determining the enthalpy and entropy of cavity formation. In view of the absence of extensive, three-dimensional hydrogen bond networks in ethanol, solvent structure effects as well as solvophobic effects are much less effective than in aqueous electrolyte solutions. In accord with our simple electrostatic analysis, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms increase with increasing salt concentration, these effects being greater for LiCl than for n-Bu_4NBr. For both salts, the rate enhancing properties are brought about by the exothermic contribution of the $\Delta S^{\ddagger}$ term. The implication is that, in contrast to water as the solvent, the variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with salt concentration is more pronounced for LiCl than for n-Bu_4NBr solutions in ethanol (Table IV).

Conclusion

To sum up the above discussion, we feel that the kinetic salt effects on the water-catalyzed hydrolysis of **1** and **2** are primarily electrostatic in nature. They seem to reflect the changes in the dynamic basicity of water molecules as a consequence of the electrostatic fields of ions which polarize the water molecules in the joint cybotactic regions of the ions and the solute. In view of the peculiarities of the water solvent, especially in the nondilute electrolyte solutions, this simple theory is limited in quantitative application. However, it is a useful framework to explain that (i) the salt effects of cations and anions operate in opposite direction and (ii) the salt effects of the ions correlate with their charge densities. In evaluating the salt effects in terms of enthalpies and entropies of activation, it is concluded that water structure effects probably modulate the electrostatic solvation effects to some extent but mainly result in $\Delta H^{\ddagger}$-$\Delta S^{\ddagger}$ compensatory behavior upon variation of the electrolyte concentration.

Experimental Section

Materials. The compounds **1** and **2**,[15] **3**,[51] and **4**[52] were prepared as described previously. The water used in all measurements was demineralized and distilled twice in an all-quartz distillation unit. Deuterium oxide (99.75% D_2O) was purchased from Merck AG

(Uvasol quality) and was used as such. 1,4-Dioxane and ethanol were also obtained from Merck AG and were of the best grade available. Dioxane was filtered through active neutral alumina in a nitrogen atmosphere before use. The solvent mixtures were made up by weight.

The salts used in all experiments were of p.a. quality and were obtained from Merck AG or Aldrich. n-Bu_4NBr was crystallized twice from a mixture of ethyl acetate–ether; the other salts were employed as such. The salt concentrations are all expressed in the aquamolality scale (moles of salt per 55.5 mol of solvent).

Kinetic Measurements. The kinetic measurements were carried out using the uv technique described previously.[15-17] All solvolysis reactions were accurate pseudo-first-order processes and the rate constants (k_{obsd}) were reproducible to within 2%. All reaction media contained small amounts of HCl (usually 10^{-3} M) in order to suppress catalysis by OH^-. Uv spectra were taken after all kinetic runs in order to ascertain that the usual solvolysis products were formed even in the most concentrated salt solutions. Activation parameters were calculated from k_{obsd} values at three to five temperatures in the region 25–45 °C. The estimated error in $\Delta H^{\ddagger}$ is ± 0.3 kcal mol^{-1} and in $\Delta S^{\ddagger}$ ± 1 eu. Although $\Delta S^{\ddagger}$ depends on the effective water concentration, only $\Delta S^{\ddagger}$ values calculated from k_{obsd} values are listed in the tables. This constitutes no serious problem however, since only *trends* in $\Delta S^{\ddagger}$ are discussed in this paper.

Thermodynamic Quantities of Transfer. The thermodynamic parameters of transfer for **3** and **4** (Table V) were obtained from solubility measurements at different temperatures following the procedure of Jolicoeur and Lacroix.[22]

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