on solvolysis of bromides where the leaving group is also a bromide ion. In solvolysis, a change in the leaving group leads to significant variation in the *m* value. For example, $m_{\text{1-AdOTs}} = 0.97$ (D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Am. Chem. Soc.*, **92**, 7300 (1970)), whereas $m_{\text{1-AdBr}} = 1.20$ at 25 °C.[19]

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Neutral Solvolysis of Covalent Arylsulfonylmethyl Perchlorates. The Kinetic Basicity of Water and Some Aliphatic Alcohols

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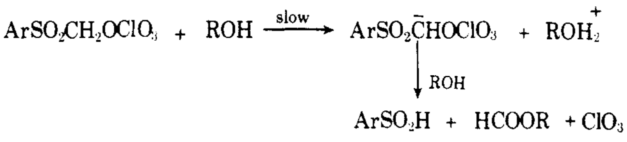
Rates and activation parameters for rate-determining deprotonation of two covalent arylsulfonylmethyl perchlorates (**1**, **2**) in water and a series of aliphatic alcohols have been determined to assess the *kinetic* basicity of these solvents. Second-order rate constants for solvent-induced deprotonation do not decrease upon decreasing solvent polarity but follow the sequence CF_3CH_2OH(TFE) < H_2O < MeOH < EtOH < *n*-PentOH < *t*-BuOH. Except for TFE, the $\Delta H^{\ddagger}$ values for solvolysis of **1** are linearly related to the gas-phase proton affinities of these solvents. The $\Delta S_2^{\ddagger}$ values parallel the cohesive energy densities of the solvents. The kinetic data are rationalized in terms of a "proton-binding" and a "solvent-ordering" process. Several factors which affect the kinetic basicity of water and organic solvents are discussed.

Recent comparisons of the gas-phase proton affinities (PA) of organic solvents with the corresponding Brönsted basicities have dramatically illustrated the crucial role of solvation effects in determining the solution basicities.[1-3] For oxygen bases such as water, alcohols, and ethers it was shown that hydrogen bonding interactions are of paramount importance in stabilizing protonated onium ions in the condensed phase.[4] These results have served as an explanation for the discrepancy between the low PA of water (165 kcal mol^{-1}) relative to that of alcohols and ethers (ca. 180–200 kcal mol^{-1}) and the relatively high equilibrium basicity of water in aqueous solutions as judged from proton exchange equilibria between water and alcohols in alcohol–water mixtures.[5] In addition, it has been shown that proton exchange of carboxylic acids is faster in water than in alcohols.[6]

For some years we have been especially interested in the kinetic basicity of solvent molecules. In this context, we now report rate constants and activation parameters for the general-base-catalyzed solvolysis of two covalent arylsulfonylmethyl perchlorates (**1**, **2**) in water and in a series of aliphatic alcohols. In the absence of other effective Brönsted bases, the solvolysis process has been shown to involve irreversible proton transfer from the substrate to the solvent[7] (primary kinetic deuterium isotope effect k_H/k_D ca. 6) and offers a quantitative but specific probe for the kinetic basicity of the solvent. Previously, the reaction has been used as a model to assess the kinetic basicities of water,[8] aqueous solvent mixtures,[9] dipolar aprotic solvents,[10] and some Brönsted bases in the presence of surfactant micelles.[11]



$$\begin{tikzcd} ArSO_2CH_2OClO_3 + ROH \arrow[r, "slow"] & ArSO_2\bar{C}HOClO_3 + RO\overset{+}{H_2} \arrow[d, "ROH"] \\ & ArSO_2H + HCOOR + ClO_3^- \end{tikzcd}$$

1, Ar = *p*-$NO_2C_6H_4$
2, Ar = *p*-$CH_3C_6H_4$
R = H, alkyl

Results and Discussion

Table I reports pseudo-first-order rate constants (k_{obsd}), activation parameters, and deuterium isotope effects for the solvolysis of **1** and **2** in water and in a series of aliphatic alcohols. All rate constants pertain to rate-determining deprotonation of the substrate by solvent molecules as indicated by the large values of the primary kinetic deuterium isotope effects (k_H/k_D) and by the observation that small amounts of acid do not influence the rates (see Experimental Section). The data summarized in Table I show that, except for 2,2,2-trifluoroethanol (TFE), water and the alcohols exhibit comparable kinetic basicities. However, direct comparison of k_{obsd} values for solvents acting as Brönsted bases is misleading because of the differences in solvent concentrations in the pure solvents. If *n* represents the number of solvent molecules which are tightly bound in the transition state for the deprotonation of **1** and **2**, k_{obsd} will be represented by $k_{n+1}[\text{solvent}]^n$. In principle, *n* may be evaluated from a plot of log k_{obsd} vs. log [solvent] when the solvent concentration is varied

Table I. Rate Constants (k_{obsd}), Activation Parameters, and Deuterium Isotope Effects for the Solvolysis of 1 and 2 in Water and in Some Alcohols (25 °C)

Compd	Solvent	$k_{obsd} \times 10^4$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k_H/k_D
1	H_2O	32.5	17.8	−10	5.6
1	D_2O	18.6	18.0	−11	1.7[a]
1	MeOH	23.4	16.5	−15	
1	EtOH	45.1	15.2	−18	
1	*t*-BuOH	64.6	14.0	−22	6.1
1	*n*-PentOH	53.7	14.7	−20	
1	TFE	Stable for a long time (>24 h)			
2	H_2O	6.05	19.1	−9	6.2
2	D_2O	3.60	19.2	−10	1.7[a]
2	EtOH	6.33	16.3	−19	6.6, 1.8[b]
2	*t*-BuOH	5.67	14.5	−25	
2	*n*-BuOH	5.46			
2	*sec*-BuOH	5.46			
2	*i*-BuOH	4.62			
2	Glycol	5.94			
1 + 2	Dioxane	Stable for a long time (>24 h)			

[a] k_{H_2O}/k_{D_2O}. [b] k_{EtOH}/k_{EtOD}.

Table II. Rate Constants (k_{obsd}) and Activation Parameters for the Ethanolysis of 1 and 2 in Dioxane–EtOH Mixtures (25 °C)

Compd	n_{EtOH}	$k_{obsd} \times 10^4$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1	1.00	45.1	15.2	−18
1	0.90	35.1	15.7	−17
1	0.80	30.3	15.7	−17
1	0.60	19.1	15.5	−19
2	1.00	5.72		
2	0.95	5.04		
2	0.90	4.91		
2	0.80	3.69		
2	0.70	2.77		

by dilution with an inert cosolvent like 1,4-dioxane (last entry of Table I). Yet, this approach can introduce errors, since it hinges on the assumption that n and k_{n+1} do not change significantly upon addition of the cosolvent. However, the solvolysis of 1 and 2 is rather insensitive to the dielectric constant of the medium.[8] Therefore, we have determined k_{obsd} values for ethanolysis of 1 and 2 in dioxane–ethanol in the mole fraction range $n_{EtOH} = 1.0–{\sim}0.6$ (Table II). Plots of log k_{obsd} vs. log [EtOH] are shown in Figure 1 and are approximately linear. The slopes of the lines, representing the factor n, are near to unity and strongly suggest that only one ethanol molecule is tightly bound in the transition state. The small changes in $\Delta H^{\ddagger}$ for 1 as a function of n_{EtOH} provides a further justification for the assumption made in the evaluation of n. For hydrolysis of 1, the factor n also amounts to 1 as demonstrated for hydrolysis in dioxane–H_2O ($n_{H_2O} = 0.2–0.6$; $n = 1.1$) and in acetonitrile–water ($n_{H_2O} = 0.3–0.6$; $n = 0.8$).[9,12,13] Second-order rate constants (k_2) as well as $\Delta S_2^{\ddagger}$ values for the hydrolysis and alcoholysis of 1 and 2 are listed in Table III. These data then lead to the following order of kinetic basicities: H_2O < MeOH < EtOH < *n*-PentOH < *t*-BuOH. Interestingly, this order accords with that found for the gas-phase proton affinities[14,15] and is, for example, *opposite* to that expected on the basis of solvent polarity expressed either in the dielectric constant (ϵ) or in solvatochromism scales like the Dimroth–Reichardt E_T values (Table III). The rate constants for solvolysis of 2 in the isomeric butanols also appear to parallel the PA values but with less precision, which may be partly due to the different water contents of these solvents[16] (see Experimental Section).

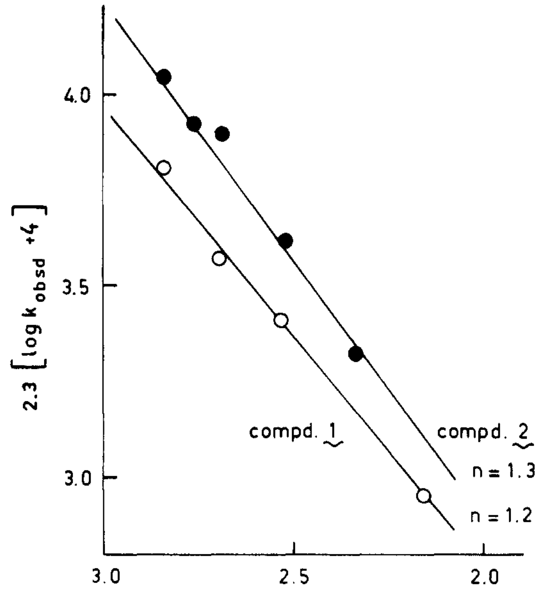


Figure 1. Plots of log k_{obsd} vs. log [EtOH] for the ethanolysis of 1 (○) and 2 (●).

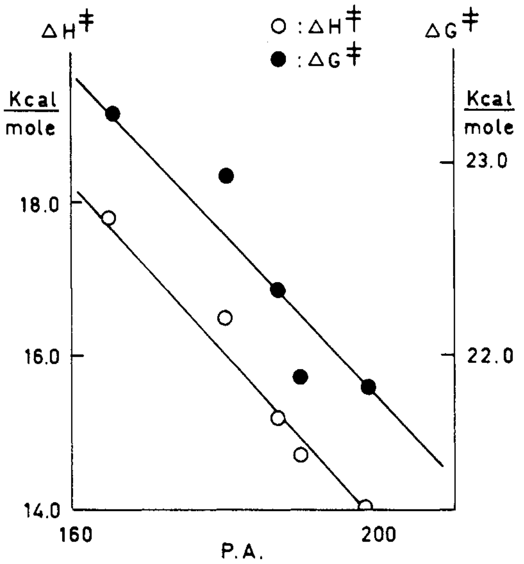


Figure 2. Plots of $\Delta G_2^{\ddagger}$ (●) and $\Delta H^{\ddagger}$ (○) for the solvolysis of 1 in water and in some alcohols vs. the gas-phase proton affinities (PA).

Figure 2 portrays the roughly linear relationship between $\Delta G_2^{\ddagger}$ and PA values for the solvolysis of 1 and the even better correlation between $\Delta H^{\ddagger}$ (independent of solvent concentration) and PAs. Based on these results, it appears likely that the rate and especially the enthalpy of activation for hydrolysis and alcoholysis of 1 and 2 predominantly reflect the bond formation between the solvent and the proton abstracted in the rate-determining step of the solvolysis process. This conclusion harmonizes with our earlier suggestion,[10] that in the transition state for deprotonation the negative charge at the α-sulfonyl carbon is highly delocalized and only weakly involved in hydrogen bonding with protic solvents. However, we expect that a significant contribution to $\Delta H^{\ddagger}$ may be provided by van der Waals–London dispersion interactions between the delocalized negative charge in the transition state and dispersion centers located at solvent molecules in the near

Table III. Rate Constants (k_2) and Activation Parameters for the Solvolysis of 1 and 2 in Water and Some Alcohols as a Function of Dielectric Constant (ϵ), Gas-Phase Proton Affinity (PA), Cohesive Energy Density (ced), and Reichardt–Dimroth E_T Value

Compd	Solvent	$k_2 \times 10^6$, L mol^{-1} s^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S_2^‡$, eu	ϵ (25 °C)	PA,[14] kcal mol^{-1}	Ced,[d] cal cm^{-3}	E_T
1	H_2O	58.5	17.8	−18	78.5	165	550.2	63.1
1	D_2O	33.7	18.0	−19	78.3			
1	MeOH	94.7	16.5	−22	32.6	180	208.8	55.5
1	EtOH	263	15.2	−24	24.3	187	161.3	51.9
1	*t*-BuOH	607	14.0	−26	9.9	198	110.3	43.9
1	*n*-PentOH	584	14.7	−24	13.9	189[a]		
2	H_2O	10.9	19.1	−17	78.5	165		
2	D_2O	6.5	19.2	−18	78.3			
2	EtOH	37.0	16.3	−24	24.3	187		
2	*t*-BuOH	53.3	14.5	−29	9.9	198		
2	*n*-BuOH	50.0			17.1	189	114.5	
2	*sec*-BuOH	50.1			15.8	197		
2	*i*-BuOH	42.7			17.7	189		
2	Glycol	33.3			37.7		213.2	
1	TFE				26.7	168		
	Dioxane				2.2		94.7	36.0
2[b]	H_2O/OH^-	7.2×10^{10}	9.8[c]	−3		~380		

[a] According to the conclusion in ref 14, the PA of *n*-PentOH is equal to the PA limit for primary alcohols. [b] k_{OH^-} in water as the solvent. [c] Calculated from rate measurements at three hydroxide ion concentrations between 10^{-3} and 5×10^{-3} M, at four different temperatures between 17 and 32 °C. [d] M. R. J. Dack, *Chem. Soc. Rev.*, **4**, 211 (1975).

vicinity. Since these interactions are determined by the polarizability of the solvent molecule, there may well exist a parallelism between the strength of these interactions and the PA values for the protic solvents listed in Table III.

Besides the "proton-binding process" in the solvolysis of 1 and 2, we can discern a "solvent-ordering process" upon formation of the transition state for deprotonation and which will be reflected in the entropy of activation ($\Delta S_2^‡$). Since the cohesive energy density (ced) of a solvent constitutes a measure for the amount of "freedom" of the solvent molecules in the condensed phase, one might expect that $\Delta S_2^‡$ values will become more negative with decreasing ced. This expectation is borne out by the data presented in Table III and supports the importance of intermolecular association between solvent molecules in determining their propensity to be transferred into their conjugate acids. A similar relationship between the magnitude of the entropy and solvent cohesion has been observed by Criss[17] for the solvation of ions in organic solvents. For proton transfer reactions involving alcohols as Brönsted bases, the entropy term may even overpower the energy contribution in determining the overall change in free enthalpy, leading to a relatively small reactivity of alcohols in acid–base reactions.[17]

Further support for the interpretation of rates of slow proton transfers in terms of a binding process and a solvent-ordering process is provided by the low kinetic basicity of TFE (despite its high ionizing power) and dioxane in the solvolysis of 1 and 2 (Table I). Although the PA of TFE (PA = 168)[19] and of dioxane[20] are higher than that of water (PA = 165), no measurable reaction occurs in either of these solvents. Most likely, this is primarily the result of the relatively weak intermolecular interactions in these solvents[21] which would cause large, negative entropies of activation upon proton transfer to these molecules. In this context we note that the rate retardation for hydrolysis of 1 in dioxane–water in the range $n_{H_2O} = 0.50–0.20$ is dominated by a decrease of $\Delta S_2^‡$. The complete absence of intermolecular hydrogen bond interaction in dioxane and the lack of hydrogen bond stabilization of the attacking dioxane molecule in the transition state for proton transfer probably both contribute to the low dynamic basicity of this solvent.

Finally, it is interesting to compare the kinetic parameters for the solvolysis reactions of 1 and 2 with those for the hydroxide ion catalyzed process. The relevant data for the hydroxide ion catalyzed hydrolysis of 2, obtained employing the stopped-flow technique, are given in Table III. The entropy of activation for this reaction is 14 eu less negative than that for the neutral hydrolysis. This result bears out the prediction that $\Delta S_2^‡$ values will increase when the interaction between the Brönsted base and solvent molecules becomes stronger. The low $\Delta H^‡$ value is in good agreement with the high PA (ca. 380)[22] of the hydroxide ion. It is not surprising to find that $\Delta H^‡_{(OH^-)}$ does not fit the relationship shown in Figure 2 because of the difference in charge of the active Brönsted bases. Although hydroxide ion may show anomalous behavior in proton transfers from carbon acids,[23] the k_{OH^-} for 2 nicely fits the Brönsted plot for hydrolysis of 2 reported previously.[7,12]

Experimental Section

Materials. The covalent perchlorates 1 and 2 were prepared as described previously.[7] The water used in the kinetic experiments was demineralized and distilled twice in an all-quartz distillation unit. Deuterium oxide (99.75% D_2O) and monodeuterioethanol (≥99.5% EtOD) were obtained from Merck (uvasol quality) and were used as such. The organic solvents (Merck) were all of the best grade available. *n*-BuOH, *sec*-BuOH, and *i*-BuOH were dried over CaH_2 and distilled twice before use. Dioxane (uvasol quality) was filtered through active, neutral alumina in a nitrogen atmosphere and was stored under nitrogen at 0 °C. The water contents of the organic solvents were determined by Karl Fischer titrations and are given in mole fraction of water: dioxane (0.0009), MeOH (0.002), EtOH (0.006), *t*-BuOH (0.0004), *n*-BuOH (0.008), *sec*-BuOH (0.01), *i*-BuOH (0.01), glycol (0.02).

Kinetic Measurements. Pseudo-first-order rate constants (k_{obsd}) for solvolysis were obtained using the UV technique described previously.[7–10] In all cases accurate first-order kinetics were observed and k_{obsd} values were reproducible to within 2%. The reaction rates in the pure solvents were not affected by the presence of 10^{-3} M $HClO_4$ or HCl. The thermodynamic quantities of activation were calculated from k_{obsd} values at three to five temperatures in the range 25–45 °C. The k_{OH^-} was measured using an Aminco-Morrow stopped-flow apparatus, connected to a data acquisition storage and retrieval system (DASAR). The data stored in the DASAR system were retrieved by recording on a W & W recorder (type 3012) to allow the calculation of the rate constant. Both dilute aqueous sodium hydroxide solutions (pH 10–11) and aqueous Borax buffers (pH 9.35) were employed.

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Aspects of Tautomerism. 6.[1a,b] Base-Catalyzed Hydrolysis of Pseudo Esters of γ-Keto Acids

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The rates of base-catalyzed hydrolysis of pseudo esters derived from γ-keto acids show strikingly poor sensitivity to the nature of the leaving group.[1a] The rates vary in the narrow range of about 12-fold as contrasted to a 10^3-fold spread of the corresponding benzoate esters. The results presented are consistent with a rate-determining formation of a tetrahedral intermediate (II) and its rapid collapse, by the cleavage of the lactone ring in a fast step.

The pseudo derivatives derived from γ- and δ-keto acids possess an interesting structural feature: the potential leaving group is not in conjugation with the carbonyl group. Therefore, the patterns of reactivity of pseudo esters may be expected to be quite different from that of normal carboxylic acid esters. In the base-catalyzed hydrolysis of carboxylic esters the leaving group has two functions, viz., (a) the conjugative function which stabilizes the ground state and decreases the carbonyl reactivity, (b) the ability to function as a leaving group. It turns out that a poor leaving group is also a good conjugative group leading to decreased reactivity of the carbonyl group on both counts.

Recently Bowden and Last[2] have reported the rates of alkaline hydrolysis of pseudo methyl esters of 8-acyl- and 8-aroyl-1-naphthoic acids and 5-formyl-1-phenanthroic acid. These authors favor a stepwise mechanism with the formation of the intermediate IV.

Newman and co-workers[3] have studied the effect of substitution in the aromatic rings with methyl groups on the rate of hydrolysis of pseudo methyl esters of *o*-benzoylbenzoic acids. Bender and co-workers[4] have studied the alkaline hydrolysis of 3-methoxyphthalide. In these studies, the effect of variation of leaving groups on the rates of hydrolysis has not been investigated. Although there is no reason to doubt that the mechanism involves the attack of hydroxide ion on the carbonyl group forming a tetrahedral intermediate, it is necessary to find out whether the reaction proceeds by a stepwise mechanism or by a concerted collapse of the lactone ring of the intermediate II (Scheme I, paths A and B).

In this paper we are reporting the results of alkaline hydrolysis of pseudo esters of *o*-benzoylbenzoic acid. The effect

Scheme I