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Acid-Catalyzed Solvolysis of Allylic Ethers and Alcohols. Competing Elimination and Substitution via a Thermodynamically “Stable” Carbocation†

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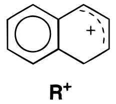
Abstract: Specific acid-catalyzed solvolysis of 1-methoxy-1,4-dihydronaphthalene (**1**-OMe) or 2-methoxy-1,2-dihydronaphthalene (**2**-OMe) in 25 vol % acetonitrile in water yields mainly the elimination product naphthalene, which is accompanied by a trace of 2-hydroxy-1,2-dihydronaphthalene (**2**-OH). No intramolecular rearrangement or formation of the alcohol **1**-OH from **1**-OMe was found. The nucleophilic selectivity between added azide ion and solvent water was measured as $k_{\mathrm{N_3}}/k_{\mathrm{HOH}} = 2.1 \times 10^4$ (ratio of second-order rate constants). The results indicate a relatively stable benzallylic carbocation toward trapping by nucleophiles ($k_{\mathrm{w}} = 1 \times 10^7$ s^{-1}). However, the elimination-to-substitution ratio with solvent water as base/nucleophile is large. Thus, in contrast to other carbocations of similar reactivity toward nucleophiles, the barrier to dehydronation is very low, $k_{\mathrm{e}} = 1.6 \times 10^{10}$ s^{-1}, and accordingly, this step does not show any catalysis from added general bases. The heats of reaction of the solvolytic eliminations of **1**-OH and **2**-OH are $\Delta H = -23.7$ and -18.4 kcal mol^{-1}, respectively, as measured by microcalorimetry.

Introduction

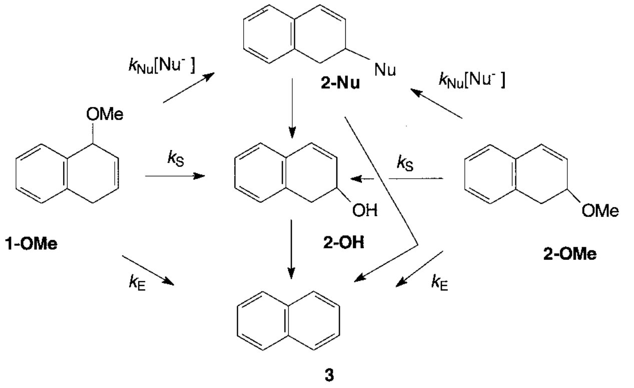
We are interested in the factors that govern the competition between substitution and elimination from carbocation intermediates. Reaction directly from an ion pair may provide predominately elimination owing to facile hydron abstraction by the leaving group.[1] Even very weakly basic leaving groups, such as halide ions, show significant kinetic basicities in many solvolytic reactions.[1,2] In contrast, solvent-equilibrated carbocations generally yield predominately substitution in nucleophilic solvents.[1−3]

We now report results on a system which provides nearly exclusively elimination product despite the intermediacy of a relatively stable benzallylic carbocation (R$^+$). Thus, the acid-catalyzed solvolysis of the ethers **1**-OMe and **2**-OMe provide naphthalene as the major product as shown in Scheme 1. A study of the dehydration of the corresponding alcohols **1**-OH and **2**-OH was recently reported by the groups of More O’Ferrall and Boyd.[4,5] They discussed the reasons for the much higher reactivity of these alcohols compared to that of 1-phenylethanol. However, it is not clear whether the predominate elimination is attributable to the large thermodynamic stability of the naphthalene product or whether there are other important factors that are responsible for the large elimination-to-substitution ratio. These reactions are of biochemical interest since naphthalene hydrates are thought to be intermediates in the mammalian metabolism of naphthalene and dihydronaphthalenes.[6]



R$^+$

Scheme 1



Reaction mechanistic studies of these allylic ethers are also interesting because they may provide insight into the reactivity and stability of carbocation−molecule pairs.[7] Such species are formed, for example, when hydronated ethers undergo carbon−oxygen heterolysis. We have found previously that they are intermediates with significant lifetimes, i.e., they are not only encounter complexes. Thus, intramolecular rearrangement of allylic ethers in aqueous solvents has been observed,[7b] and the substitution reaction of a tertiary ether with solvent water is faster than diffusional separation.[7f]

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Table 1. Second-Order Rate Constants for the Acid-Catalyzed Reactions of **1**-OMe, **2**-OMe, **1**-OH, and **2**-OH at 25 °C

	ethers		alcohols	
solvent	k_H^{1-OMe}, $M^{-1}\,s^{-1}$	k_H^{2-OMe}, $M^{-1}\,s^{-1}$	k_H^{1-OH}, $M^{-1}\,s^{-1}$	k_H^{2-OH}, $M^{-1}\,s^{-1}$
MeCN−water[a]	53.2[b,e]	0.128[b,f]	47[c,g] 46[d,g]	0.173[b,h]
glycerol−water[a]			254[c,i] 258[d,i]	1.22[c,j] 1.22[d,j]
water			240[k]	1.8[k]

[a] 25 vol % organic solvent in water. [b] Measured by HPLC. [c] Measured by UV spectrophotometry (UV). [d] Measured by microcalorimetry (MC). [e] Cf. Figure S1a. [f] Cf. Figure S1b. [g] 0.1 M acetate buffer, pH 4.18 (UV) and pH 5.19 (MC). [h] 0.1 M formate buffer, pHs 3.38 and 4.15. [i] 0.05 M phosphate buffer, pH 6.60. The rate constants at 15 and 45 °C were measured (UV) as 126 and 1475 M^{-1} s^{-1}, respectively. [j] 0.1 M acetate buffer, pH 4.18. The rate constants at 15 and 45 °C were measured (UV) as 0.328 and 9.33 M^{-1} s^{-1}, respectively. [k] Data from ref 4.

The results of the present work are consistent with a common solvent-equilibrated carbocation intermediate, but some reaction through ion−molecule pairs cannot be excluded. The mechanistic details of the reactions are discussed.

Results

The acid-catalyzed solvolysis of 1-methoxy-1,4-dihydronaphthalene (**1**-OMe) or 2-methoxy-1,2-dihydronaphthalene (**2**-OMe) in 25 vol % acetonitrile in water at 25 °C yields mainly naphthalene (**3**) along with a small amount of 2-hydroxy-1,2-dihydronaphthalene (**2**-OH) (Scheme 1). No traces of the rearranged ether product **2**-OMe or the alcohol 1-hydroxy-1,4-dihydronaphthalene (**1**-OH) were found in the reactions of **1**-OMe. The kinetics of the reactions were studied by a sampling high-performance liquid chromatography procedure or by following the appearance of **3** as a function of time by UV spectrophotometry. The same methods were used to study the kinetics of the acid-catalyzed solvolysis of **1**-OH and **2**-OH.

The rate of solvolysis is, as expected, proportional to the acidity of the medium, i.e., [H_3O^+], which is shown for **1**-OMe and **2**-OMe in Figure S1. The rate of solvolysis at constant buffer ratio is not a function of buffer concentration (Figure S2), which indicates that the acid catalysis is of specific rather than of general type. Moreover, the absence of buffer catalysis also indicates that there is no general base catalysis involved in the rate-limiting step. The measured rate constants are shown in Table 1.

The effect of salts on the reactions is relatively large in 25 vol % acetonitrile in water as shown in Figure 1 for **1**-OMe with acetate buffer. Salt effects have also been studied at a higher pH using phosphate buffer at a constant concentration of 0.5 M NaCl (Figure 2). Similar behavior was observed for **2**-OMe (plots not shown). The effect of salt concentration in 50 vol % methanol in water is much smaller, which is shown in Figure 2 for azide ion. As expected, one more product, **2**-OMe, is formed in this solvent mixture.

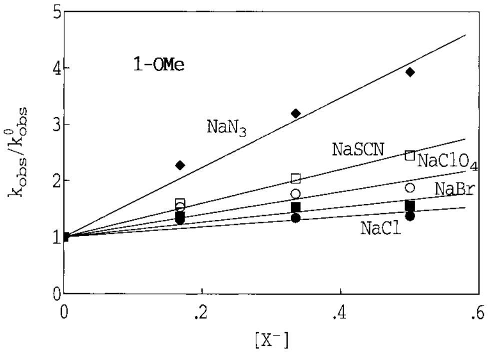

Figure 1. Effect of added salts on the rate of solvolysis of **1**-OMe in the presence of 0.10 M acetate buffer (buffer ratio 1.0) in 25 vol % acetonitrile in water at 25 °C.

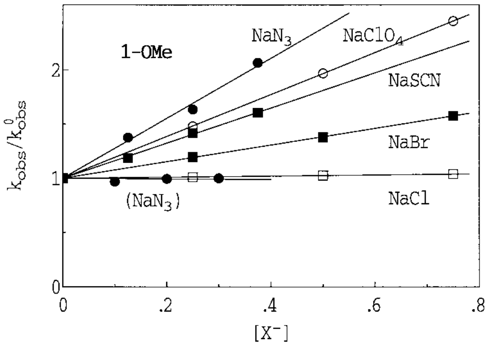

Figure 2. Effect of added salts on the rate of solvolysis of **1**-OMe in 25 vol % acetonitrile in water (and in 50 vol % methanol in water, lower line) at 25 °C in the presence of 0.50 M NaCl, 0.075 M phosphate buffer at pH 6.23.

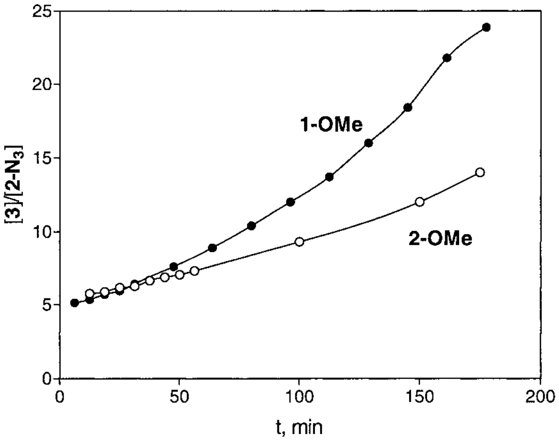

Figure 3. Increase in the elimination-to-substitution ratio [**3**]/[**2**-N_3] for **1**-OMe and **2**-OMe, respectively, with reaction time. Reaction conditions: 3.00 M azide buffer, [HN_3]/[N_3^-] = 4.71.

Addition of azide ion gives rise to the substitution product **2**-N_3 (Scheme 1), but no trace of **1**-N_3 is observed. However, it is not possible to exclude that it is formed initially since allylic azides are known to isomerize very rapidly.[8] Addition of 0.3 M NaN_3 yields only 5% of **2**-N_3. The same initial fraction was obtained from all the ethers and alcohols.

The azide product **2**-N_3 is not stable but slowly reacts to give naphthalene (**3**) as the final product. The rate constant of decomposition of **2**-N_3 was measured in a separate experiment as 470 × 10^{-6} s^{-1} (see the Experimental Section). Figure 3 shows the variation of the product ratio [**3**]/[**2**-N_3] for **1**-OMe

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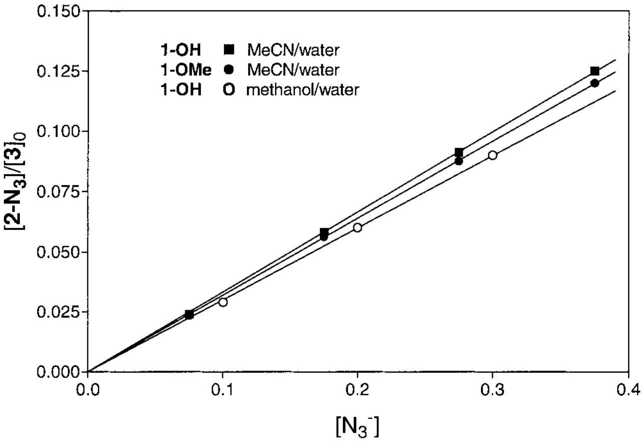


Figure 4. Increase in the substitution-to-elimination ratio [**2**-N_3]/[**3**]$_0$, i.e., ratios extrapolated to zero reaction time, with NaN_3 concentration for reaction of **1**-OH and **1**-OMe, respectively. Reaction conditions: 0.50 M NaCl, 25 °C, 0.075 M phosphate buffer in 25 vol % acetonitrile in water at pH 6.30 and in 50 vol % methanol in water at pH 6.13.

Table 2. Effect of Salt on the Elimination-to-Substitution Ratio [**3**]/[**2**-N_3]$_0$ for Acid-Catalyzed Solvolysis of **1**-OH in 25 vol % Acetonitrile in Water at 25 °C

salt (0.75 M)[a]	[**3**]/[**2**-N_3]$_0$[b]	salt (0.75 M)[a]	[**3**]/[**2**-N_3]$_0$[b]
none	9.0 ± 0.6	NaCl	12.5 ± 1.4
$NaClO_4$	11.0 ± 1.2	NaBr	13.3 ± 1.5
NaOAc	12.0 ± 1.2	NaSCN	16.0 ± 1.6

[a] 0.075 M phosphate buffer, pH 6.23. [b] Extrapolated to time zero; 0.25 M NaN_3.

and **2**-OMe as a function of time. The product ratio was extrapolated to time zero to obtain the reaction rate ratio $k_{N_3}[N_3^-]/k_E$ for nucleophilic substitution with azide, $k_{N_3}[N_3^-]$, and elimination, k_E. The intercepts of the two plots are 5.0 and 5.5, i.e., the same within experimental error, which suggests a common intermediate for the reactions of these isomeric substrates. Extrapolated ratios for **1**-OMe and **1**-OH are plotted versus azide ion concentration in Figure 4, which also includes data for **1**-OH in 50 vol % methanol in water. The slopes of these plots, which are very similar, correspond to the ratios of the second-order reaction rate constants of addition of azide ion and the pseudo-first-order rate constants of dehydronation of the carbocation intermediate. The slope of the plot for **1**-OMe is 0.32 M^{-1}.

No substitution product with any other strong nucleophile was detected, not even with thiocyanate ion. The reason is presumably that **2**-SCN is formed but that it is not stable and rapidly yields naphthalene and a small amount of **2**-OH as the final product. Another possibility is that the small amount of **2**-SCN is not detected owing to coelution with the large naphthalene product peak during the HPLC analysis.

The effect of salt on the product ratio [**3**]/[**2**-N_3] extrapolated to time zero was studied with **1**-OH. The ratio increases with more nucleophilic salts as shown in Table 2. The product ratio [**3**]/[**2**-OMe] for solvolysis of **1**-OH in 50 vol % methanol in water was also found to change by addition of salt (Table 3).

The nucleophilic selectivity toward azide ion and solvent components is very large. The results for **1**-OMe are shown in Table 4. The alcohols **1**-OH and **2**-OH show the same results. The rate-constant ratios are ratios of second-order rate constants calculated by means of eq 1.

$$k_{Nu}/k_{HOH} = ([\mathbf{2}\text{-Nu}]/[\mathbf{2}\text{-OH}])/([Nu]/[H_2O]) \qquad (1)$$

Table 3. Effect of Salt on the Elimination-to-Substitution Ratio [**3**]/[**2**-OMe]$_0$ for Acid-Catalyzed Solvolysis of **1**-OH in 50 vol % Methanol in Water at 25 °C

salt (0.50 M)[a]	[**3**]/[**2**-OMe]$_0$[b,c]	salt (0.50 M)[a]	[**3**]/[**2**-OMe]$_0$[b,c]
none	1100	NaBr	1522
$NaClO_4$	1315	NaSCN	1782
NaOAc	1205	NaN_3[d]	2356
NaCl	1454		

[a] 0.05 M phosphate buffer, pH 6.23. [b] Measured after 20−30 min of reaction. No significant amount of solvolysis of the product **2**-OMe has occurred after this short reaction time. [c] Estimated maximum error ± 10%. [d] 0.30 M.

Table 4. Nucleophilic Selectivities Expressed as Ratios of Second-Order Rate Constants (Eq 1)

substrate	k_{N_3}/k_{HOH}	k_{MeOH}/k_{HOH}	k_{EtOH}/k_{HOH}
1-OMe	2.1×10^4[a]	~3.6[b]	~2.8[c]

[a] 25 vol % acetonitrile in water. [b] Calculated as the ratio of [**3**]/[**2**-OH] and [**3**]/[**2**-OMe] measured in aqueous acetonitrile and in 50 vol % methanol in water, respectively. [c] Calculated as the ratio of [**3**]/[**2**-OH] and [**3**]/[**2**-OEt] measured in aqueous acetonitrile and in 50 vol % ethanol in water, respectively.

Table 5. Heat of Reactions for the Dehydration of **1**-OH and **2**-OH at 25 °C

substrate	P_0,[a] μW	ΔH, kcal mol^{-1}
1-OH[b]	20.0	−23.7 ± 0.4[d]
2-OH[c]	12.0	−18.4 ± 0.2[e]

[a] Heat effect at time zero (extrapolated). [b] Concentration of 0.76 mM. [c] Concentration of 0.64 mM. [d] Average of 12 runs at pH 6.10−6.80. [e] Average of six runs at pH 4.18.

Activation Parameters. Activation parameters were calculated for the solvolyses of **1**-OH and **2**-OH in 25 vol % glycerol in water at constant pH, rate constants measured at 15, 25, and 45 °C (Table 1). The activation enthalpies and entropies were calculated from slopes of Arrhenius plots and the free energies of activation at 25 °C. The results for **1**-OH are $\Delta G^\ddagger = 14.2$ kcal mol^{-1}, $\Delta H^\ddagger = 14.5$ kcal mol^{-1}, and $\Delta S^\ddagger = 1$ eu and for **2**-OH are $\Delta G^\ddagger = 17.3$ kcal mol^{-1}, $\Delta H^\ddagger = 19.6$ kcal mol^{-1}, and $\Delta S^\ddagger = 7$ eu.

Calorimetric Measurements. The acid-catalyzed solvolyses of the alcohols have also been studied by heat-flow microcalorimetry. These reactions, as described above, yield exclusively naphthalene and naphthalene along with a trace of **2**-OH, respectively. Thus, the heats produced from both reactions are attributable to formation of the elimination product.

The reactions were carried out in 25 vol % glycerol in water. Glycerol was used instead of acetonitrile to minimize disturbances from trace amounts of vaporization of the organic solvent from the sealed reaction flasks. A time period of 40−60 min after initiation of the reaction was required for thermal equilibration. The observed decreases in heat flow reflect pseudo-first-order kinetic behavior of the reactions. The measured rate constants agree well with those obtained with the spectrophotometric technique (Table 1). The measured reaction enthalpies are given in Table 5.

Discussion

Rate-Limiting Carbocation Formation. The alcohols **1**-OH and **2**-OH and the corresponding ethers **1**-OMe and **2**-OMe are highly reactive. For example, acid-catalyzed solvolysis of **1**-OH yielding naphthalene is almost 10^{11} times faster than the corresponding reaction of 1-phenylethanol.[4,9] The formation of the benzallylic carbocation (R^+) from the ethers is rate-limiting as shown by the absence of general acid−base catalysis (Figure S2). This is in accord with the results of More O'Ferrall and co-workers, who did not find any general catalysis for **1**-OH and **2**-OH in aqueous acetic acid buffers.[4] One-step concerted elimination directly from the hydronated substrates, or rate-limiting elimination via the carbocation, would require such catalysis. The higher reactivity of **1**-OMe compared to that of the isomeric **2**-OMe is consistent with stepwise reactions of the corresponding hydronated ethers since concerted base-promoted elimination reactions are unfavored compared to their 1,2-counterparts due to the requirement for a large number of changes in bonding occurring at a single reaction step.

The faster reaction of **1**-OH than of 1-phenylethanol reflects that the acid-catalyzed dehydration of the latter does not involve rate-limiting formation of the cation but undergoes rate-limiting elimination. However, this difference in rate-limiting step has been estimated to account for only a factor of about 700 of the total factor of ca. 10^{11}.[4] Other factors such as enhanced resonance in the cyclic cation and the effect of a vinyl substituent have been suggested to be of importance.[4]

Salt effects on acid-catalyzed solvolysis reactions are more complex than those on uncatalyzed solvolysis since they consist of the effect on the fast hydronation step combined with the effect on the ionization to the carbocation−molecule complex. The observed effect of salts on the reaction rate is relatively large in aqueous acetonitrile but is small in 50 vol % methanol in water (Figures 1 and 2). Similar behavior has been seen before for uncatalyzed solvolysis reactions of substrates with charged leaving groups.[10] The absence of an increase in the rate of reaction of **1**-OMe in the presence of added azide ion in aqueous methanol suggests that bimolecular reactions are not significant.

The pK_R for the pseudo acid−base equilibrium for cation hydration (eqs 2 and 3) is a measure of the thermodynamic stability of R^+.

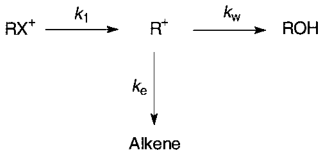
$$R^+ + H_2O \underset{k_H}{\overset{k_w}{\rightleftarrows}} ROH + H^+ \qquad (2)$$

$$K_R = k_w/k_H = [ROH][H^+]/[R^+] \qquad (3)$$

The rate constant (k_H, Table 1) for the acid-catalyzed solvolysis of **2**-OH in 25 vol % acetonitrile in water is 0.173 $M^{-1}\ s^{-1}$. This rate constant, combined with the rate constant for addition of water to R^+ of $k_w = 1.0 \times 10^7\ s^{-1}$ (vide infra) yields $pK_R = -7.8$. The corresponding rate constant (k_w) for reaction of R^+ to give **1**-OH is not known, but it is reasonable to assume that it is at least 10 times smaller than that for giving **2**-OH, which yields $pK_R \geq -6.3$. These values could be compared with the corresponding parameter for the 1-(4-methylphenyl)ethyl carbocation of $pK_R = -12.8$, measured in 50 vol % trifluoroethanol in water.[3]

Reactivity of the Benzallylic Carbocation. In contrast to most other solvolysis reactions through relatively stable carbocation intermediates, the dehydronation of the carbocation is much faster than the addition reaction with solvent or added powerful nucleophiles. The elimination-to-substitution ratio k_E/k_S with solvent water is as large as 1600. Is this abnormal relative reactivity solely due to the large stability of the naphthalene product, or is the addition of nucleophiles to the carbocation slower than normal?[11] This issue is addressed in the following.

Scheme 2



The rate constant (k_w) for reaction of the carbocation with water to give **2**-OH (Scheme 2) has been measured by the "azide-clock" method assuming that the reaction with azide ion is diffusion-controlled with a rate constant of $5 \times 10^9\ M^{-1}\ s^{-1}$.[3,12] The rate constant measured in this manner is $k_w = 1.0 \times 10^7\ s^{-1}$. The same result was obtained by starting from either **1**-OMe, **1**-OH, or **2**-OMe. This rate constant is not unusually small and is consistent with a diffusion-limited reaction with azide anion since direct measurements of rate constants using flash photolysis have shown that carbocations with $k_w > 1 \times 10^5\ s^{-1}$ react with azide ion in a diffusion-controlled process in aqueous acetonitrile.[12] The reactivity of R^+ is on the same order as that of $(4\text{-}MeC_6H_4)_2CH^+$, for which a rate constant of $k_w = 3.2 \times 10^7\ s^{-1}$ was directly measured.[12]

Only one azide product is observed in the solvolysis of **1**-OMe and **1**-OH. A plausible trace of **1**-N_3 formed is expected to rapidly isomerize to **2**-N_3 since allylic azides are known to isomerize quickly.[8] A single allylic azide isomer product has been observed previously in solvolytic reactions.[13] The carbocation shows discrimination between the nucleophiles water, methanol, and ethanol of $k_{MeOH}/k_{HOH} \sim 3.6$ and $k_{EtOH}/k_{HOH} \sim 2.8$, ratios of second-order rate constants (eq 1 and Table 4). The values are "normal" for a relatively stable carbocation.[1] In summary, there is no indication for an unusually slow reaction of the benzallylic carbocation with nucleophiles but, of course, conclusive evidence could only be obtained through direct measurement of the rate constants.

In accord with the results discussed above, we attribute the unusually large elimination-to-substitution ratio to an unusually fast dehydronation of the carbocation intermediate. The azide-trapping method yields a rate constant for hydron abstraction from R^+ of $k_e = 1.6 \times 10^{10}\ s^{-1}$ in the aqueous acetonitrile solvent (Figures 3 and 4). This rate constant is unusually large for a thermodynamically stable carbocation such as the benzallylic R^+. For example, it is 10^4 times larger than the elimination rate constant for 1-(4-methylphenyl)ethyl carbocation measured in 50 vol % trifluoroethanol in water,[3] despite the fact that the difference in pK_R values (vide supra) indicates a great difference in thermodynamic stability of the cations.

The fast hydron abstraction reflects the large thermodynamic stability of the naphthalene product (see next section) and should correspond to a very small amount of hydron transfer in the transition state. Thus, the transition state of the hydron-abstraction step is expected to be very reactant-like, i.e., close to the benzallylic carbocation in structure (Brønsted $\beta \sim 0$). Accordingly, the effect of added general bases on the elimination-to-substitution ratio is not large. For example, the presence of 0.75 M acetate ion in the aqueous acetonitrile gives only a

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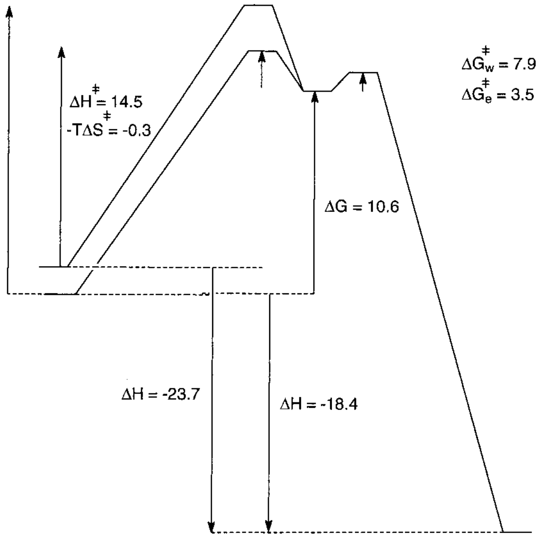
Scheme 3



small increase in the ratio [**3**]/[**2**-N_3] (Table 2) compared to no salt addition. However, this effect is not significantly larger than that for perchlorate ion. Nevertheless, there is a small increase with more powerful nucleophiles (Table 2). A similar increase in the amount of elimination was also observed in 50 vol % methanol in water where the ratio of naphthalene-to-ether formation was studied (Table 3).

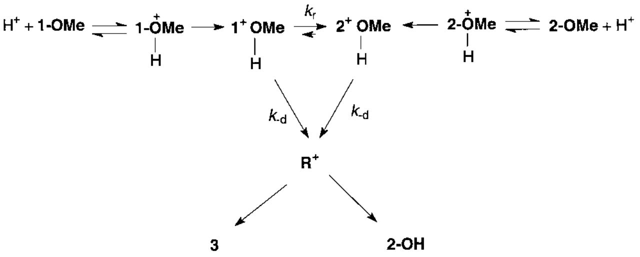
In principle, the catalysis could be due to either hydron abstraction within the ion pair or a first formation of the covalent material (**2**-Nu) which undergoes a concerted one-step 1,2-elimination with the solvent acting as the hydron-abstracting base. Catalysis from added chloride ion has been observed previously for the dehydronation of ferrocenyl-stabilized carbocations in 50 vol % acetonitrile in water.[14]

Mapping of Reaction Energies. The microcalorimetric measurements show large heats of reaction: $\Delta H = -23.7$ and -18.4 kcal mol^{-1} for **1**-OH and **2**-OH, respectively. These values agree well with the estimated change in free energy of $\Delta G^{\ddagger} \sim -20$ kcal mol^{-1} ($K \sim 10^{15}$) for dehydration of naphthalene hydrates in aqueous solution.[4,5] In contrast, 1-phenylethanol is more stable than styrene by about 2 kcal mol^{-1} ($K = 0.025$).[9a]

The difference in enthalpy of $\Delta\Delta H = 5.3$ kcal mol^{-1} for **1**-OH and **2**-OH is close to the difference in activation enthalpy, $\Delta\Delta H^{\ddagger} = 5.1$ kcal mol^{-1}, but the difference in reactivity is smaller (Table 1; 208-fold in glycerol−water, $\Delta\Delta G^{\ddagger} = 3.2$ kcal mol^{-1}). The difference in energy of the rate-limiting transition states of these reactions may be attributable to a more delocalized transition state of the reaction of **2**-OH. This more advanced transition state corresponds to a larger entropy of reaction. The measured energies are shown in Scheme 3.

Ion−Molecule Pair Intermediates. The complexes initially formed by the carbon−oxygen cleavage are the carbocation−methanol pairs as indicated in Scheme 4. However, our results do not give any information as to whether these complexes are discrete intermediates, i.e., if they have significant lifetimes. We have previously found indications in several systems for the intermediacy of ion−molecule pairs with methanol as the leaving group.[7b,f,g] For example, results were reported that strongly suggest that delocalization of charge in the carbocation lags behind the cleavage of the carbon−oxygen bond.[7f]

Scheme 4



The failure to observe formation of **1**-OH and **2**-OMe from **1**-OMe is presumably due to the fact that the cleavage of the carbon−oxygen bond is accompanied by extensive delocalization of charge in this system. This delocalization is expected to decrease the stability of $\mathbf{1}^{+}$OHMe, which favors diffusional separation by *increasing* the barrier for collapse of the ion−molecule pair back to covalent material as well as *increasing* the barrier for direct substitution of the ion−molecule pair with a water molecule.

Experimental Section

General Procedures. NMR spectra were recorded for $CDCl_3$ solutions with a Varian XL 300 spectrometer. Chemical shifts are indirectly referenced to tetramethylsilane via the solvent signal (chloroform-d_1, 7.26 and 77.0 ppm). The high-performance liquid chromatography analyses were carried out with a Hewlett-Packard 1090 liquid chromatograph equipped with a diode-array detector on an Inertsil 5 OSD-2 (3 × 100 mm) reversed-phase column. The chromatography was performed isocratically using acetonitrile in water as the mobile phase. The reactions were studied at constant temperature in a HETO 01 PT 623 thermostat bath. The UV spectrophotometry was performed on a Kontron Uvicon 930 spectrophotometer equipped with an automatic cell changer kept at constant temperature using a thermostated water bath. The reaction solutions for the kinetic experiments were prepared by mixing acetonitrile, glycerol, or methanol with water at room temperature, ca. 22 °C. The pH was measured before and after reaction using a Radiometer PHM82 pH meter with an Ingold glass microelectrode. The pH values given are those measured before mixing with the organic solvent. The microcalorimetric experiments were carried out with a dual-channel calorimeter (Thermometrics Thermal Activity Monitor 2277). The signals were recorded on both a two-channel potentiometric recorder (LKB 2210) and a HP 3390 digital device.

Materials. Previously reported procedures were followed for preparation of the substrates 1-hydroxy-1,4-dihydronaphthalene (**1**-OH),[15] 1-methoxy-1,4-dihydronaphthalene (**1**-OMe),[15] and 2-hydroxy-1,2-dihydronaphthalene (**2**-OH).[16] 2-Methoxy-1,2-dihydronaphthalene (**2**-OMe) was prepared from **2**-OH by the same procedure as was used for synthesis of **1**-OMe. After purification the substrates were free from traces of isomeric impurities, and the ethers did not contain any of the corresponding alcohol. Methanol and acetonitrile were of HPLC grade. All other chemicals were of reagent grade and used without further purification.

Kinetics and Product Studies: HPLC Procedure. The reactions were initiated by addition of a few microliters of the substrate dissolved in acetonitrile to a 2-mL HPLC flask containing 1.2 mL of the thermostated reaction solution to give a substrate concentration of 0.1−0.2 mM. The reaction flask was sealed with a gastight PTFE septum and placed in a thermostated aluminum block in the HPLC apparatus. At appropriate intervals, samples were automatically injected onto the column and analyzed. The rate constants for the disappearance of the substrates were calculated from plots of substrate peak area versus time by means of a nonlinear regression computer program. Very good

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[14] Bunton, C. A.; Carrasco, N.; Cully, N.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1859.

[15] Moss, R. J.; Rickborn, B. *J. Am. Chem. Soc.* **1986**, *51*, 1992.

[16] (a) Bamberger, E.; Lodter, W. *Justus Leibigs Ann. Chem.* **1895**, *288*, 100. (b) Jeffrey, A. M.; Jerina, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 4048.

pseudo-first-order behavior was seen for all of the reactions studied. The separate rate constants for the elimination and substitution reactions were calculated by combination of product composition data, obtained from the peak areas and the relative response factors determined in separate experiments, with the observed rate constants.

The azide product **2**-N_3 is not stable but slowly reacts to give naphthalene as the final product. The rate constant for this decomposition was measured after complete solvolysis of **1**-OH with azide buffer at low pH. After neutralization, the disappearance of **2**-N_3 was followed by HPLC.

UV Spectrophotometric Procedure. The reactions were run in 3-mL standard quartz cells using the above-mentioned equipment. Addition of a few microliters of a concentrated solution of the substrate in acetonitrile to 2.5 mL of reaction solution gave an initial concentration of the substrate in the reaction flask of 0.1 mM. The increases in absorbance at 275 and 300 nm, respectively, were followed as a function of time and the pseudo-first-order rate constant calculated by a nonlinear regression computer program.

Microcalorimetric Procedure. This technique has the advantage that both kinetic data and reaction heats are obtained from the same kinetic experiment. The reactions were run in parallel in the two channels, both composed of a sample compartment and a reference compartment. Glass vials (3 mL) were used as reaction and reference vessels. All four vessels were filled at the same time with 2.5 mL of premixed buffer solution (glycerol−water). After this step, 20 μL of substrate in acetonitrile was added to the two reaction vessels while 20 μL of pure acetonitrile was added to the reference vessels. The vials were sealed with gastight PTFE septa and slowly introduced into the compartments of the instrument for about 15 min of prethermostating. They were than lowered further down into the detection chambers. After a total time of 30−45 min it was possible to start recording the first-order heat-flow decay. The reactions were followed for at least 10 half-lives.

The microcalorimeter was statically calibrated after a kinetic experiment using the reaction solutions. The time constant of the instrument was found to be 240 s, i.e., no correction for this parameter was necessary for calculation of the rate constants of the reaction heat decay. Very good first-order rate constants (k_{obs}) were measured. These agree well with those measured in the kinetics using the UV spectrophotometric technique (Table 1).

The extrapolated heat flow at time zero (P_0) was used for calculation of the reaction heat (ΔH) according to eq 4:

$$P_0 = \Delta H k_{obs} n \tag{4}$$

where n is the amount of substrate (mol) in the reaction vial.

The estimated errors are considered as maximum errors derived from maximum systematic errors and random errors.

Acknowledgment. We thank Prof. Rory More O'Ferrall for comments and the Swedish Natural Science Research Council for supporting this work.

Supporting Information Available: The effect of pH and buffer concentration on the rate of solvolysis of **1**-OMe and **2**-OMe (Figures S1 and S2) (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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