Solvent Nucleophilicity

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Abstract: The rates of the reactions of benzhydrylium ions (diarylcarbenium ions) with solvent mixtures of variable composition (water/acetonitrile, methanol/acetonitrile, ethanol/acetonitrile, ethanol/water, and trifluoroethanol/water) have been determined photometrically by conventional UV−vis spectroscopy, stopped-flow methods, and laser flash techniques. It has been shown that the first-order rate constants follow the previously published relationship $\log k(20\,°C) = s(N + E)$, where E is an empirical electrophilicity parameter, N is an empirical nucleophilicity parameter, and s is a nucleophile-specific slope parameter. From plots of $\log k$ versus E of the benzhydrylium ions are derived the solvent nucleophilicity parameters s and N, the latter of which are designated as N_1 to emphasize that their use in the quoted correlation equation gives rise to first-order rate constants. A linear correlation between N_1 and Kevill's solvent nucleophilicity N_T based on *S*-methyldibenzothiophenium ions is reported, which allows one to interconvert the two sets of data. Because the N_1 values are directly comparable to the previously reported nucleophilicity parameters N for π-systems (www.cup.uni-muenchen.de/oc/mayr/), the systematic design of Friedel−Crafts reactions with solvolytically generated carbocations becomes possible.

Introduction

The development of quantitative scales of solvent nucleophilicity has intrigued chemists for several decades.[1,2] Such scales are important for the theory of nucleophilic substitutions and for designing syntheses where the solvent may compete with other nucleophiles for the electrophile under consideration.

In 1948, Grunwald and Winstein presented the relationship (1), which expresses the rates of S_N1 solvolyses of substrates RX by a substrate-specific parameter m ($m = 1$ for *tert*-butyl chloride) and a solvent-specific parameter, the solvent-ionizing power Y ($Y = 0$ for 80% aqueous ethanol).[3]

$$\log(k/k_0)_{25\,°C} = mY \qquad (1)$$

where k and k_0 are the first-order rate constants for the solvolysis of RX in a given solvent and the standard solvent 80% aqueous ethanol (v/v), respectively, at 25°C. Equation 1 holds for S_N1 reactions with a rate-determining ionization step where nucleophilic solvent participation is absent.[4]

Three years later, Winstein, Grunwald, and Jones reported that S_N2 reactions proceed considerably faster in aqueous alcohols than in mixtures of acetic acid and formic acid of equal ionizing power Y and assigned these differences to the higher

Scheme 1
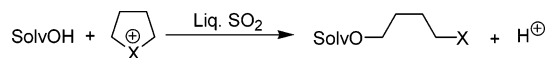
nucleophilicities of alcohols.[5] In the extended Grunwald−Winstein eq 2,[6] the electrophilic term mY of eq 1 is accompanied by the nucleophilic term lN, where l is the sensitivity toward changes in solvent nucleophilicity N.

$$\log(k/k_0)_{RX} = mY + lN \qquad (2)$$

While the solvent-ionizing power Y can easily be determined by investigating substrates which solvolyze without nucleophilic solvent participation (limiting S_N1, $l = 0$), it is difficult to find reactions which are entirely controlled by the nucleophilic term, that is, substitutions with $m = 0$.

Peterson and Waller[7] derived a scale of nucleophilicities of solvent molecules from the rates of reactions of solvent molecules with tetramethylenehalonium ions in liquid sulfur dioxide (Scheme 1).

More widely employed is the N_{OTs} scale. Schadt, Bentley, and Schleyer defined the sensitivity of solvolysis rates of methyl tosylate on solvent nucleophilicity as $l = 1$.[8] With the assumption of equal nucleophilicities of acetic and formic acid, as derived from Peterson's and Waller's work, Bentley and Schleyer concluded that the sensitivity of methyl tosylate

† Universität München.
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(3) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846−854.
(4) More exactly, eq 1 would hold for any situation where nucleophilic solvent participation is equal in both the substrate under consideration and the standard, *tert*-butyl chloride.

(5) Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700−2707.
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solvolyses on solvent-ionizing power is $m = 0.3$. Substitution of this value into eq 2 yields eq 3 which has widely been used for the determination of solvent nucleophilicities.[8]

$$N_{OTs} = \log (k/k_0)_{MeOTs} - 0.3 Y_{OTs} \qquad (3)$$

where k is the rate constant for the solvolysis of methyl tosylate in the solvent under consideration, and k_0 is the rate constant for the solvolysis of methyl tosylate in 80% aqueous ethanol (v/v).

While the choice of $m = 0.3$ for methyl tosylate solvolyses was still being debated and other factors, for example, $m = 0.55$, had been proposed,[9] Kevill recognized that substrates with neutral leaving groups provide a superior tool for determining solvent nucleophilicity. In analogy to earlier studies by Swain,[10] the solvolysis rates of 1-adamantyldimethylsulfonium triflate were found to be affected by solvent variation by less than a factor of 7, while the solvolysis rates of 1-adamantyl tosylate varied by 7 powers of 10 within the same group of solvents. Consequently, it was concluded that in solvolyses of oxonium and sulfonium ions, that is, substrates with neutral leaving groups, the contribution of solvent-ionizing power can be neglected, and Kevill employed the solvolysis rates of the S-methyldibenzothiophenium ion (S_N2 reactions) as the basis of the solvent nucleophilicity scale N_T (eq 4).[11]
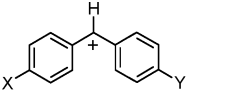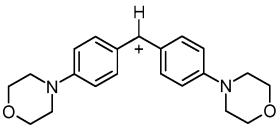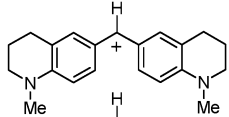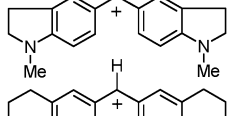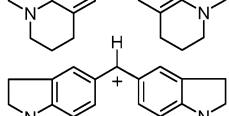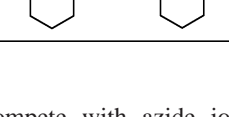
$$N_T = \log(k/k_0)_{MeDBTh^+} \qquad (4)$$

where k is the rate constant for the solvolysis of the S-methyldibenzothiophenium ion (MeDBTh$^+$) in the solvent under consideration, and k_0 is the rate constant for the solvolysis of the S-methyldibenzothiophenium ion (MeDBTh$^+$) in 80% aqueous ethanol (v/v).

Although the solvent nucleophilicity parameters N_{OTs} and N_T defined by eqs 3 and 4 show fairly good correlations with each other as well as with solvent nucleophilicities derived from solvolyses of other methylsulfonium or triethyloxonium ions,[2] they are relative parameters, which are not linked to other scales of nucleophilicity. The ongoing controversy on the role of nucleophilic solvent participation is highlighted by the title of a recent *J. Am. Chem. Soc.* article: "Is the *tert*-Butyl Chloride Solvolysis the Most Misunderstood Reaction in Organic Chemistry?".[12]

The development of fast kinetic methods provides a possibility for the direct measurement of solvent nucleophilicity. Thus, carbocations have been generated by laser flash induced heterolysis of suitable precursors, and the rate of decay of these carbocations in various solvents reflects solvent nucleophilicity, decoupled from solvent-ionizing power.[13] Similar information has also been obtained with Jencks' and Richard's azide clock method which derives solvent nucleophilicity from the ability

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Scheme 2. Abbreviations and Electrophilicity Parameters E of Benzhydrylium Ions

	X	Y	E^a
(pcp)$_2$CH$^+$	Cl	Cl	6.02
Ph$_2$CH$^+$	H	H	5.90
(pfp)PhCH$^+$	F	H	5.60
(tol)PhCH$^+$	CH$_3$	H	4.59
(tol)$_2$CH$^+$	CH$_3$	CH$_3$	3.63
(pop)PhCH$^+$	OPh	H	2.90
(ani)PhCH$^+$	OCH$_3$	H	2.11
(ani)(tol)CH$^+$	OCH$_3$	CH$_3$	1.48
(ani)(pop)CH$^+$	OCH$_3$	OPh	0.61
(ani)$_2$CH$^+$	OCH$_3$	OCH$_3$	0.00
(fur)$_2$CH$^+$			−1.36
(pfa)$_2$CH$^+$	N(Ph)CH$_2$CF$_3$	N(Ph)CH$_2$CF$_3$	−3.14
(mfa)$_2$CH$^+$	N(CH$_3$)CH$_2$CF$_3$	N(CH$_3$)CH$_2$CF$_3$	−3.85
(dpa)$_2$CH$^+$	NPh$_2$	NPh$_2$	−4.72
(mor)$_2$CH$^+$			−5.53
(mpa)$_2$CH$^+$	N(Ph)CH$_3$	N(Ph)CH$_3$	−5.89
(dma)$_2$CH$^+$	N(CH$_3$)$_2$	N(CH$_3$)$_2$	−7.02
(pyr)$_2$CH$^+$	N(CH$_2$)$_4$	N(CH$_2$)$_4$	−7.69
(thq)$_2$CH$^+$			−8.22
(ind)$_2$CH$^+$			−8.76
(jul)$_2$CH$^+$			−9.45
(lil)$_2$CH$^+$			−10.04

^{a} From ref 15.

of solvents to compete with azide ions for solvolytically generated carbocations.[14]

We have recently suggested the employment of benzhydrylium ions as reference electrophiles (Scheme 2) for the quantitative comparison of nucleophiles of widely differing structures and reactivities.[15]

As described in detail in refs 15 and 16, nucleophilicity parameters N and s, as defined by eq 5, can be obtained by plotting log k(20 °C) for the reactions of a certain nucleophile

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Scheme 3
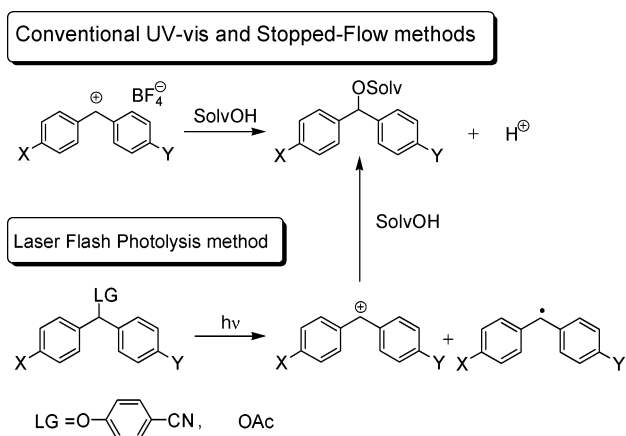
with a series of electrophiles of Scheme 2 versus the corresponding electrophilicity parameters, E.

$$\log k(20\ °C) = s\ (N + E) \qquad (5)$$

We have now used this method for characterizing the nucleophilic reactivities of a series of common solvents and solvent mixtures, and we will compare the solvent nucleophilicities thus obtained to the nucleophilicities of other n-, π-, and σ-nucleophiles.

For the sake of clarity, nucleophilicity parameters of solvents and solvent mixtures which refer to first-order rate constants (k_1) are designated as N_1. For solvent mixtures where only one component of the solvent is acting as the nucleophile, they may be converted into ordinary N values (referring to second-order rate constants) by subtraction of the logarithm of the molarity ($\log [Nuc]$) of the nucleophilic component. For the solvent mixtures investigated in this work, $[Nuc] = 2-55$ mol L^{-1}; that is, the N values referring to second-order rate constants are $0.3-1.7$ units smaller than N_1.

Most solvent nucleophilicity parameters N_1 and s presented in this work are based on the UV–vis photometric detection of the decay of the benzhydrylium ion concentrations with three independent kinetic methods (Scheme 3): conventional UV–vis spectrometry ($\tau_{1/2} > 10$ s), stopped-flow (10 s > $\tau_{1/2} > 10^{-3}$ s), and laser flash techniques (10^{-3} s > $\tau_{1/2} > 10^{-7}$ s). The mutual agreement of the rate constants determined by using these three methods corroborates the reliability of the present data.

Experimental Section

Materials. Benzhydrylium tetrafluoroborates,[15] benzhydryl 4-cyanophenolates,[13c,17] and benzhydryl acetates[13c,17] were prepared as previously described.

Water was distilled and passed through a Milli-Q water purification system. Alternatively, HPLC grade water was distilled before use. Methanol and ethanol were distilled over CaH$_2$. 2,2,2-Trifluoroethanol was stored over molecular sieves (3 Å) and distilled over CaSO$_4$. Acetonitrile was dried with molecular sieves (3 Å) or distilled over diphenylketene.

Synthesis of Bis(2,3-dihydrobenzofuran-5-yl)methyl Tetrafluoroborate (fur)$_2$CH$^+$BF$_4^-$. Bis(2,3-dihydrobenzofuran-5-yl)methanol

(15) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.
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Table 1. Independence of the First-Order Decay of (thq)$_2$CH$^+$ in 50W50AN of the Concentration of DABCO/DABCO−H$^+$ BF$_4^-$ (1/1) Buffer Additive

[(thq)$_2$CH$^+$], mol L^{-1}	[DABCO], [DABCO–H$^+$], mol L^{-1}	k_{obs}, s^{-1}
6.84×10^{-6}	9.44×10^{-4}	1.24×10^{-3}
8.57×10^{-6}	2.37×10^{-3}	1.22×10^{-3}
8.06×10^{-6}	3.33×10^{-3}	1.21×10^{-3}
7.84×10^{-6}	4.33×10^{-3}	1.22×10^{-3}
8.39×10^{-6}	5.79×10^{-3}	1.22×10^{-3}
		average $k = 1.22 \times 10^{-3}$ s^{-1}

(fur)$_2$CHOH[18] (0.87 g, 3.2 mmol) was dissolved in a mixture of 50 mL of dry ether and 2.2 mL (17 mmol) of propionic anhydride. A 54% etheral solution of HBF$_4$·OEt$_2$ (1.34 g, 8.24 mmol) was added. The mixture was stirred at room temperature for 1 h and cooled with an ice bath for 20 min. The precipitate was filtered off under nitrogen and washed successively with cold, dry ether and cold, dry pentane. The residue was dried in vacuo to yield 0.79 g of a deep-violet powder (2.3 mmol, 72%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 3.49 (t, $J = 8.6$ Hz, 4H), 5.01 (t, $J = 8.6$ Hz, 4H), 7.18 (d, $J = 8.7$ Hz, 2H), 8.12 (d, $J = 8.7$ Hz, 2H), 8.27 (s, 2H), 8.72 (s, 1H, Ar$_2$CH).

Kinetics. The benzhydrylium salts used in this study are colored substances whose absorption maxima have been reported previously.[15,19,20] For the investigation of the reactions of the benzhydrylium ions with solvents, stock solutions of benzhydrylium tetrafluoroborates in acetonitrile were prepared, then combined with the nucleophilic solvent, and the disappearance of the benzhydrylium absorbances was followed photometrically. For investigations of the nucleophilicities of trifluoroethanol/water mixtures, stock solutions of benzhydrylium tetrafluoroborates ($E < -3$) in trifluoroethanol were employed.

Reactions with $\tau_{1/2} > 10$ s were monitored by conventional UV–vis measurements using fiber optics and an immersion probe as described previously.[20−22]

For the stopped-flow measurements, the stock solutions of the benzhydrylium salts in acetonitrile or TFE were mixed with the nucleophilic solvents in the stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst2 software) in ratios of 1/1 or 1/10, and the decay of the benzhydrylium absorbance was followed as described previously.[15,20,23]

The rates of rapid reactions ($\tau_{1/2} < 1$ ms) were determined with laser flash photolytically generated benzhydrylium ions which were obtained from diarylmethyl 4-cyanophenolates or diarylmethyl acetates (Scheme 3).[13b] Irradiation by laser flash in a quartz cell was carried out with a Continuum PL9010 Nd:YAG laser flash apparatus ($\lambda = 266$ nm; power/puls ca. 50 mJ). An Osram XBO 150W xenon lamp was used as a light source for the detection in the UV–vis region.

All rates were measured at 20 °C (±0.2 °C for stopped-flow and conventional experiments, ±1 °C for laser flash experiments). First-order rate constants k_{obs} (s^{-1}) were obtained by least-squares fitting of the absorbance data to the single-exponential curve $A_t = A_0 \exp(-k_{obs}t) + C$. As a consequence of the poor solubility of the benzhydrylium tetrafluoroborates, benzhydryl 4-cyanophenolates, and benzhydryl acetates in some of the solvent mixtures, up to 1% of a cosolvent (CH$_3$CN) was employed.

Results

When the benzhydrylium ions were exposed to the aqueous or alcoholic solvent mixtures specified in Tables 1 and 2 as

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Table 2. First-Order Rate Constants (s⁻¹) for the Reactions of Water/Acetonitrile Mixtures with Benzhydrylium Ions at 20 °C[a]

cation	E	W	91W9AN	80W20AN	67W33AN	50W50AN	33W67AN	20W80AN	10W90AN
Ph_2CH^+	5.90					1.33×10^9 [b]			
$(tol)_2CH^+$	3.63			3.2×10^7 [c]	3.2×10^7 [c]	3.28×10^7	3.47×10^7	3.06×10^7	2.37×10^7
$(ani)PhCH^+$	2.11	1.9×10^6 [d]		2.0×10^6 [c]	2.1×10^6 [c]	1.84×10^6	1.91×10^6	1.87×10^6	1.83×10^6
$(ani)(tol)CH^+$	1.48	7.8×10^5 [d]	7.99×10^5	8.2×10^5 [c]	9.1×10^5 [c]	8.55×10^5	8.95×10^5	8.29×10^5	6.81×10^5
$(ani)_2CH^+$	0.00	9.44×10^4	9.55×10^4	1.0×10^5	1.3×10^5 [c]	1.04×10^5	1.01×10^5	9.82×10^4	9.87×10^4
$(fur)_2CH^+$	−1.36								7.11×10^2
$(pfa)_2CH^+$	−3.14		9.36×10^1	4.93×10^1	4.96×10^1	3.62×10^1	3.39×10^1	3.32×10^1	1.42×10^1
$(mfa)_2CH^+$	−3.85		4.39	3.98	4.47	3.78[e]	3.58	3.62	1.57
$(dpa)_2CH^+$	−4.72					4.44	4.12	3.97	1.56
$(mor)_2CH^+$	−5.53		6.73×10^{-1}	4.93×10^{-1}	4.13×10^{-1}	3.31×10^{-1} [e]	2.85×10^{-1}	2.51×10^{-1}	8.03×10^{-2}
$(mpa)_2CH^+$	−5.89		3.31×10^{-1}	2.84×10^{-1}	2.83×10^{-1}	2.52×10^{-1}	2.24×10^{-1}	2.17×10^{-1}	8.08×10^{-2}
$(dma)_2CH^+$	−7.02	2.06×10^{-2}							
$(pyr)_2CH^+$	−7.69	5.57×10^{-3} [e]	4.29×10^{-3}	3.77×10^{-3}	4.05×10^{-3}	4.33×10^{-3}			
$(thq)_2CH^+$	−8.22	2.20×10^{-3} [e]	1.66×10^{-3}	1.23×10^{-3}	1.17×10^{-3}	1.22×10^{-3}	1.28×10^{-3}		

[a] Compositions of solvents are given as (v/v); W = water, AN = acetonitrile. [b] From ref 13d; because of the proximity of the diffusion limit, this value was not used for the correlation. [c] From ref 13c. [d] From ref 17 at 25 °C. [e] Reference 20.

well as in Tables S1−S5 in the Supporting Information, an exponential decay of the benzhydrylium absorbances was observed. Probably because of solubility problems, the reactions of $(dpa)_2CH^+$ and $(pfa)_2CH^+$ with trifluoroethanol/water = 20/80 or 10/90 could not be described by single-exponential functions, and rate constants for these reactions are not given in Table S3. For the same reason, Table 2 (and Table S1) does not give rate constants for the reactions of $(dpa)_2CH^+$ with aqueous acetonitrile containing more than 50% water.

Laser flash photolysis of the benzhydryl 4-cyanophenolates or acetates[24] results in heterolytic or homolytic cleavage of the $Ar_2CH−O$ bond as shown in Scheme 3. Because the absorption maxima of the benzhydryl radicals are at considerably lower wavelengths than those of the benzhydryl cations,[19] the concomitant formation of both species does not affect the observation of the exponential decay of the benzhydryl cation absorbances during the reactions with the nucleophilic solvent.

As described for acetonitrile/water mixtures in Tables 1 and 2, and for many other solvents and solvent mixtures in Tables S1−S5 of the Supporting Information, the solvent nucleophilicities were examined with benzhydrylium ions of widely differing reactivity. Generally, rate constants covering a range of 7−10 powers of 10 were employed for characterizing each of the solvent systems.

Rate constants for the reactions of acetonitrile/water mixtures with the weak electrophiles $(thq)_2CH^+$ ($E = −8.22$) and $(pyr)_2CH^+$ ($E = −7.69$) were obtained with a conventional UV−vis spectrometer by injecting concentrated solutions of the corresponding benzhydrylium tetrafluoroborates in acetonitrile into the solvent mixtures under consideration. Table 1 shows that the rate constants for the first-order decay of $(thq)_2CH^+$ in 50W50AN mixtures are independent of the concentrations of DABCO/DABCO−H⁺ buffer additives.

Because an analogous behavior has been observed for the consumption of $(pyr)_2CH^+$ in acetonitrile/water and of $(ind)_2CH^+$ and $(thq)_2CH^+$ in ethanol/water mixtures (see Supporting Information), it is concluded that the reaction of the benzhydrylium ion with the solvent molecule and not the successive proton transfer is rate-determining (Scheme 4). This conclusion is in accord with Ritchie's report that the reaction of crystal

Scheme 4
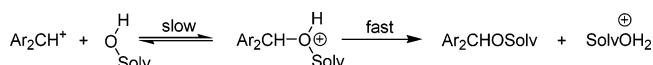
violet ($E = −11.3$)[20] with H_2O and D_2O does not show a kinetic isotope effect.[25]

If more electrophilic benzhydrylium ions are employed, the rates of deprotonation of the oxonium ions in Scheme 4 can be assumed to remain almost unaffected, while the reverse reactions, that is, the regeneration of the benzhydrylium ions, must become slower. Consequently, we can conclude that all reactions monitored by stopped-flow and laser flash techniques in this work proceed via rate-determining attack of the solvent nucleophiles at the benzhydrylium ions.

The reactions of benzhydrylium ions of electrophilicity −6 < E < −1 with acetonitrile/water mixtures were determined with stopped-flow techniques by combining solutions of benzhydrylium tetrafluoroborates in acetonitrile with water or acetonitrile/water mixtures to yield the solvent mixtures listed in Table 2. Because the stopped-flow instrument used in this work does not allow us to employ mixing ratios >10:1, we were unable to study solvent mixtures with water or alcohol contents >91%.

Benzhydrylium ions of $E \geq 0$ have been generated by 20-ns laser pulses in the corresponding solvent mixtures, and their decay has been followed by UV−vis spectroscopy. Some of these data were already available in the literature as indicated in Table 2.

Figure 1 shows that plots of rate constants (log k_1) determined by the three different methods versus the empirical electrophilicity parameters E give linear correlations. This proves the consistency of the data obtained by the independent methods as well as the applicability of eq 5 for describing the reactions of carbocations with these solvents. The fact that some of the data depicted in Figure 1 as well as in 35 analogous correlations (shown in the Supporting Information) have been taken from the literature is an additional confirmation for the reliability of our data, and vice versa.

Slopes and intercepts of the correlations in Figure 1 (and the analogous correlations shown in the Supporting Information) yield the nucleophilicity parameters N_1 and s given in Table 3. In some cases, carbocations of different electrophilicity were

(24) Most experiments were performed with 4-cyanophenolates. Benzhydrylium acetates were used in highly aqueous solutions, where the solubility of the benzhydryl 4-cyanophenolates is low, or in solvents of low nucleophilicity, where the recombination of the benzhydrylium ions with 4-cyanophenolate anion is fast as compared to the reaction of Ar_2CH^+ with the solvent.

(25) Ritchie, C. D.; Skinner, G. A.; Badding, V. G. *J. Am. Chem. Soc.* **1967**, *89*, 2063−2071.
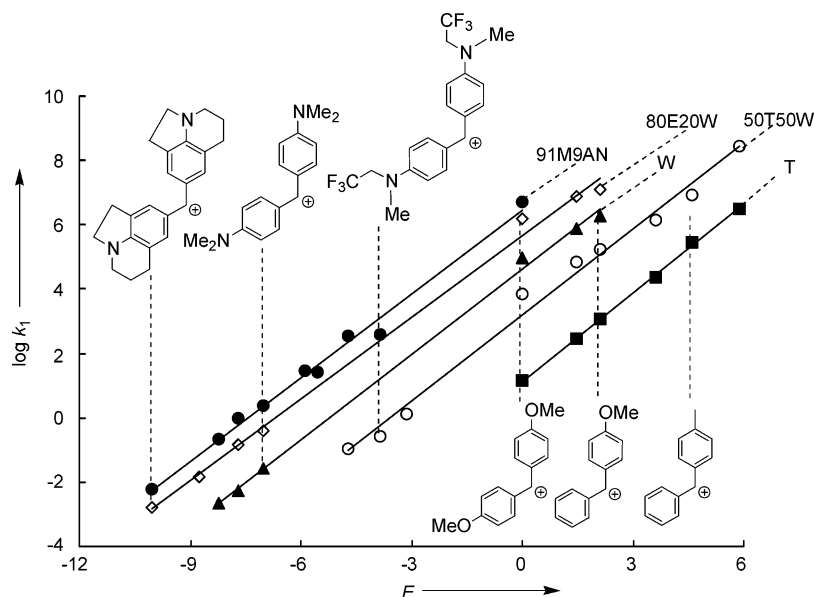
Figure 1. Plots of log k_1 for the decay of benzhydrylium ions in several solvents versus the electrophilicity parameters E of the benzhydrylium ions (20 °C). Mixtures of solvents are given as (v/v), solvents: M = methanol, E = ethanol, W = water, T = trifluoroethanol, AN = acetonitrile.

Table 3. Nucleophilicity (N_1) and Slope (s) Parameters for Solvents

solvent[a]	N_1	s
W	5.20	0.89
91W9AN	5.16	0.91
80W20AN	5.04	0.89
67W33AN	5.05	0.90
50W50AN	5.05	0.89
33W67AN	5.02	0.90
20W80AN	5.02	0.89
10W90AN	4.56	0.94
T	1.23	0.92
90T10W	2.93	0.88
80T20W	3.20	0.88
60T40W	3.42	0.90
50T50W	3.57	0.89
40T60W	3.77	0.88
20T80W	4.78	0.83
10T90W	5.04	0.90
E	7.44	0.90
90E10W	7.03	0.86
80E20W	6.68	0.85
60E40W	6.28	0.87
50E50W	5.96	0.89
40E60W	5.81	0.90
20E80W	5.54	0.94
10E90W	5.38	0.91
91E9AN	7.10	0.90
80E20AN	6.94	0.90
67E33AN	6.74	0.89
50E50AN	6.37	0.90
33E67AN	6.06	0.90
20E80AN	5.77	0.92
10E90AN	5.19	0.96
M	7.54	0.92
91M9AN	7.45	0.87
80M20AN	7.20	0.89
67M33AN	7.01	0.91
50M50AN	6.67	0.90
33M67AN	6.38	0.92
20M80AN	6.04	0.94
10M90AN	5.55	0.97

[a] Mixtures of solvents are given as (v/v), solvents: M = methanol, E = ethanol, W = water, T = trifluoroethanol, AN = acetonitrile.

found to react with equal rates, corresponding to $k = 10^7$ s^{-1}. Because this value appeared to be the limit of the instrumenta-

tion employed, these rate constants were not used for the calculation of the correlation equations.

The nucleophilicity parameter for methanol listed in Table 3 can be compared to that derived from Ritchie's rate constants for the reactions of methanol with tritylium ions and tropylium ions, $N_1 = 6.02$ and $s = 1.01$.[20] These values, which have explicitly been labeled as "Approximate Parameters" in Table 7 of ref 20, can now be revised. It should be noted, however, that our previous guess[20] was able to reproduce the rate constants for the reactions of benzhydrylium ions with methanol reported here, with an accuracy of a factor of 50. Table S6 in the Supporting Information shows that the rate constants given in Table 2 and in Tables S1–S5 can be reproduced by the reactivity parameters in Table 3 with a standard deviation of a factor of 1.82.

Discussion

The close similarity of all s parameters in Table 3 implies that the relative nucleophilicities of these solvents and solvent mixtures are fairly independent of the carbocation electrophilicities. As a consequence, the data set reported in this work might also be described by constant selectivity relationships of the Ritchie type.[26] However, because the s parameters in Table 3 are considerably larger than those of most other nucleophiles investigated by Ritchie ($s \approx 0.6$ for amines, alkoxides, etc.),[20] it is not possible to treat the whole set of nucleophilicity parameters by Ritchie's equation.[26] We, therefore, base the following discussion on the nucleophilicity parameters N_1 and s as derived from eq 5.

In agreement with a previous report by McClelland,[13c] the nucleophilicities of acetonitrile/water mixtures remain almost constant when the extent of water exceeds 20% (v/v, Figure 2).

In contrast, the nucleophilicities of methanol/acetonitrile and of ethanol/acetonitrile mixtures increase steadily with the amount

(26) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354. (b) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170–1179. (c) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239–2250.
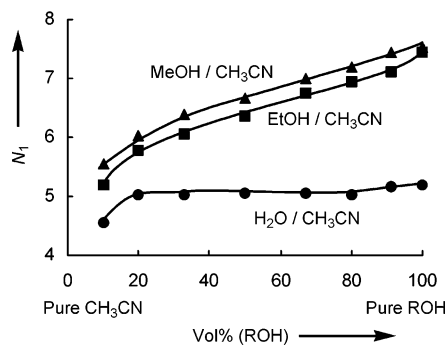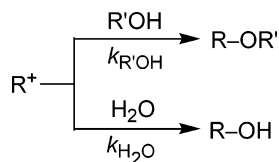
Figure 2. Dependence of the nucleophilicity N_1 on the composition of mixtures of acetonitrile with water, methanol, or ethanol.
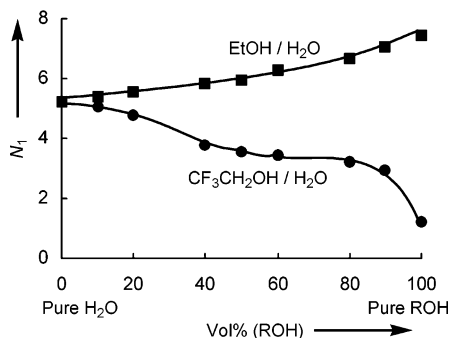
Figure 3. Dependence of the nucleophilicity N_1 on the composition of water/alcohol mixtures.

**Scheme 5.** Selectivities of Carbocations in Alcohol/Water Mixtures

of alcohol. While pure methanol and pure ethanol possess approximately the same nucleophilicity, methanol/acetonitrile mixtures are more nucleophilic (by ca. 0.3 logarithmic units) than the corresponding ethanol/acetonitrile mixtures. Figure 2 shows a remarkable increase of nucleophilicity from 90% ethanol/10% acetonitrile to pure ethanol, resulting in almost equal reactivities of pure methanol and pure ethanol. Because variation of solvent composition over such wide ranges causes significant medium effects, we will not discuss the formal second-order rate constants.

Figure 3 shows that the nucleophilicity of ethanol/water mixtures grows with increasing content of alcohol while the nucleophilicity of trifluoroethanol/water mixtures decreases with increasing content of alcohol. The steep decrease from 90% trifluoroethanol to pure trifluoroethanol is particularly obvious.

Product ratios obtained from solvolytically generated carbocations in alcohol/water mixtures (Scheme 5) have been the topic of extensive investigations[27] and have been reviewed by Ta-Shma and Rappoport.[27r]

It has been found that the ratio $k_{R'OH}/k_{H_2O}$ derived from product analysis depends on solvent polarity and generally decreases slightly from 50% aqueous alcohols to pure alcohols.[27r] Combination of the absolute rate constants for the decay of laser flash solvolytically generated benzhydrylium ions $(ani)_2CH^+$ with the product ratios yields the individual rate constants $k_{R'OH}$ and k_{H_2O} as defined in Scheme 5. For ethanol/water mixtures,
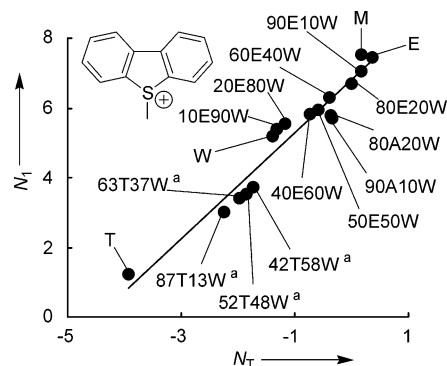
Figure 4. Relationship between nucleophilicity parameters N_1 and N_T from reactions with benzhydrylium ions and the S-methyldibenzothiophenium ion, respectively. Mixtures of solvents are given as (v/v), solvents: M = methanol, E = ethanol, W = water, T = trifluoroethanol, A = acetone. For N_T, see ref 32. For N_1 of 90A10W and 80A20W, see ref 33. (a) The nucleophilicities N_1 were obtained by interpolating data for aqueous trifluoroethanol from Table 3.

it has been shown, for example, that both individual rate constants, k_{EtOH} and k_{H_2O}, grow by a factor of approximately 10^2 when 5% ethanol/95% water was gradually replaced by 95% ethanol/5% water.[27r] The rate constants do not increase uniformly, however: While the ratio k_{EtOH}/k_{H_2O} was close to 1 in 95% ethanol as well as in 95% water, k_{EtOH}/k_{H_2O} reached a broad maximum of 4.6 in 15−50% aqueous ethanol. Because of the reported dependence of the selectivities $k_{R'OH}/k_{H_2O}$ on the medium,[27r] we have not calculated individual rate constants in this work.

How do the solvent nucleophilicities N_1 derived from the reactions with benzhydrylium ions (Table 3) compare to those solvent nucleophilicities previously derived from S_N2 reactions of methyl sulfonium ions and methyl tosylate? The good correlation shown in Figure 4 demonstrates that nucleophilicities toward carbocations and toward methyl sulfonium ions (S_N2 reactions)[2] are closely related, which justifies Kevill's choice of methyl sulfonium ions as substrates for determining nucleophilic solvent participation in S_N1 reactions. Correlation eq 6 indicates that nucleophile variation has a considerably stronger influence on the reactivities toward carbocations than toward methyl sulfonium ions.

$$N_1 = 1.51N_T + 6.79, \quad n = 17, \quad R^2 = 0.948 \qquad (6)$$

An analogous conclusion has previously been drawn by Bunting,

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who found a linear correlation between the aminolysis rates of methyl 4-nitrobenzenesulfonate (S_N2 reaction) and the corresponding rates of amine additions to the 1-methyl-4-vinylpyridinium ion with a slope of 2.27 (=1/0.44).[28] Bunting's and Richard's reports of linear correlations between Ritchie's N_+-parameters (nucleophilicities toward carbocations)[26] and Swain's and Scott's *n*-parameters (nucleophilicities toward CH_3Br)[29] with slopes of 2 also indicate that variations of nucleophiles affect reactivities toward electrophilic C_{sp^2} centers to a larger extent than toward electrophilic C_{sp^3} centers.[28,30] In accordance with these findings, *l*-values (according to eq 2) greater than 1 have been found for solvolyses of chloroformate when nucleophilic addition to the carbonyl group was rate-determining.[31]

Because linear correlations between N_T, N'_T, N_{OTs}, and N'_{OTs} have previously been reported,[2] it is not surprising that the nucleophilicity parameters N_1 derived from reactions with benzhydrylium ions in this work also correlate linearly with N'_T, N_{OTs}, and N'_{OTs} (Figures S1–S3, Supporting Information).

Because of the good correlation between N_1 and N_T shown in Figure 4, we suggest the employment of eq 6 for estimating N_1 of further solvent mixtures from reported N_T values (Table 4). Although the data obtained in this way have to be considered as approximate, they are most useful for designing syntheses in these solvents.

The linear correlation shown in Figure 4 implies that the solvent nucleophilicities N_1 toward carbocations reported in this work are controlled by the same factors as the solvent nucleophilicities N_T toward methylsulfonium ions. A major advantage of the new parameters N_1 is that they can be combined with the electrophilicity parameters E of carbocations, using eq 5, so as to estimate absolute lifetimes of carbocations which are produced solvolytically in aqueous or alcoholic solutions.[33]

Because $s \approx 0.9$ for all solvents investigated (Table 3), eq 5 predicts that carbocations have a half-life $\tau_{1/2} > 10^{-10}$ s^{-1} if $E + N_1 < 11$. As 10^{-10} s^{-1} is the time needed for solvent reorganization, one can conclude that in 80% aqueous ethanol ($N_1 = 6.68$), carbocations with $E < 4.5$ will be thermally equilibrated, while in trifluoroethanol ($N_1 = 1.23$), thermal equilibration will already be reached for carbocations of $E < 10$. Typical E values for carbocations are ca. 8.5 (for $(CH_3)_3C^+$),[34] 5.9 (for Ph_2CH^+),[15] and 0.5 (for Ph_3C^+).[20] It should be noted, however, that eq 5 has been reported to be limited to second-order rate constants $<10^8$ L mol^{-1} s^{-1}. For faster reactions, the magnitude of the rate constants will be overestimated because of the flattening of the correlation curves.[34] As a consequence, thermal equilibration of the intermediate carbocations may also occur if the sum ($E + N_1$) is slightly higher than 11.

Table 4. Approximate Solvent Nucleophilicity Parameters (N_1) for Solvent Mixtures Calculated by Eq 6

solvent[a]	N_T[b]	N_1[c]
70E30W	−0.20	6.5[d]
30E70W	−0.93	5.7[d]
95A5W	−0.49	6.1
70A30W	−0.42	6.2
60A40W	−0.52	6.0
50A50W	−0.70	5.7
40A60W	−0.83	5.5
30A70W	−0.96	5.3
20A80W	−1.11	5.1
10A90W	−1.23	4.9
80D20W	−0.46	6.1
70D30W	−0.37	6.2
60D40W	−0.54	6.0
50D50W	−0.66	5.8
40D60W	−0.84	5.5
20D80W	−1.12	5.1
97T3W[e]	−3.30	1.8
80T20W[e]	−2.19	3.5
80T20E	−1.76	4.1
60T40E	−0.94	5.4
50T50E	−0.64	5.8
40T60E	−0.34	6.3
20T80E	0.08	6.9
97H3W[e]	−5.26	−1.2
90H10W[e]	−3.84	1.0
70H30W[e]	−2.94	2.4
50H50W[e]	−2.49	3.0
HCO$_2$H	−2.44	3.1
CH$_3$CO$_2$H	−1.78	4.1

[a] Unless otherwise stated, mixtures of solvents are given as (v/v), solvents: M = methanol, E = ethanol, W = water, T = trifluoroethanol, A = acetone, D = dioxane, H = hexafluoro-2-propanol. [b] From ref 2. [c] A slope parameter of $s = 0.9$ is recommended for these solvents (compare *s* parameters in Table 3). [d] Not by using eq 6, but by interpolating data for aqueous ethanol from Table 3. [e] Mixtures of solvents are given as (w/w).

The flattening of the log k versus E correlations for $k > 10^8$ L mol^{-1} s^{-1} also prevents the calculation of the exact point, where the enforced change from S_N1 to S_N2 mechanisms is taking place. According to Jencks, this point is related to the lifetimes of intermediates, which cannot be shorter than the duration of a bond vibration (ca. 10^{-13} s).[35] Having in mind the flattening of the correlation lines for $s(E + N) > 8$,[34] one can only derive a lower limit and conclude that solvolysis with $s(E + N) < 13$ will not proceed via enforced S_N2 type mechanisms.

A further advantage of the N_1 parameters listed in Table 3 is their direct comparability to the previously published N parameters of π-systems[15,16,36–39] and hydride donors.[15,40–43] Thus, it becomes possible to predict nucleophiles which can intercept

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(32) Nucleophilicities N_T of solvent mixtures (v/v) from ref 2: 0.37 (E), 0.17 (M), 0.16 (90E10W), 0 (80E20W), −0.35 (90A10W), −0.37 (80A20W), −0.39 (60E40W), −0.58 (50E50W), −0.74 (40E60W), −1.16 (20E80W), −1.31 (10E90W), −1.38 (W), −1.71 (42T58W = 50T50W, w/w), −1.85 (52T48W = 60T40W, w/w), −1.98 (63T37W = 70T30W, w/w), −2.25 (87T13W = 90T10W, w/w), −3.93 (T).
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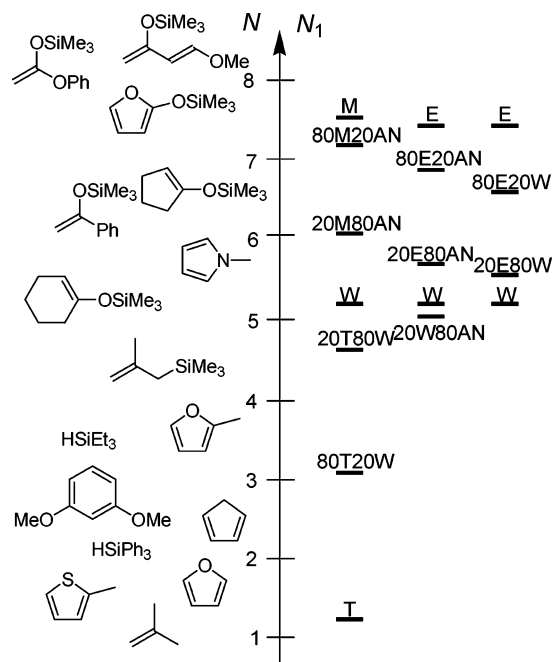
Figure 5. Comparison of the nucleophilicity parameters N_1 of solvents to the N parameters of typical π-systems and hydride donors. Mixtures of solvents are given as (v/v), solvents: M = methanol, E = ethanol, W = water, T = trifluoroethanol, AN = acetonitrile.

solvolytically generated carbocations in alcoholic or aqueous solutions as previously determined for one example by Richard.[44] If the nucleophiles on the left side of Figure 5 are employed in concentrations of [Nuc] = 1 mol L^{-1}, the calculated second-order rate constants become numerically identical to the pseudo-first-order rate constants ($k_{1\Psi} = k_2$[Nuc]) with the consequence that the N and N_1 parameters on both sides of Figure 5 become directly comparable.

If the s parameters are neglected in a first approximation, 1 M solutions of the nucleophiles on the left of Figure 5 may be expected to react equally fast with carbocations as the solvents on the right of Figure 5. As a consequence, carbocations may be trapped by 1 M solutions of nucleophiles of $N > 1.2$ if trifluoroethanol is used as the solvent and by nucleophiles of $N > 7.5$ if they are generated in methanol. This analysis is not perfectly correct, however, because it neglects the solvent dependence of the N parameters. Although we have shown that the rates of the reactions of carbocations with neutral π-nucleophiles and neutral hydride donors only slightly depend on

solvent polarity (chloroform, dichloromethane, acetonitrile, nitromethane),[21,36,40,45] there is evidence that π-nucleophilicity increases somewhat in protic solvents.[44] As a consequence, it is not only possible to trap carbocations by π-nucleophiles and hydride donors which are located above the corresponding reaction media in Figure 5 but also by those located slightly below the corresponding solvents. In agreement with this conclusion, Richard had previously reported that carbocations which are solvolytically generated in 50% aqueous acetonitrile ($N_1 = 5.05$) can be trapped by π-nucleophiles which possess N parameters greater than 6 even when they are used in lower concentrations (0.01–0.1 mol L^{-1}).[44] Kitagawa's trapping of fullerenyl cations (E ca. 7–8)[46] by anisole ($N = -1.18$, $s = 1.20$)[16] in 9/1 (v/v) anisole/trifluoroethanol must be due to the high s parameter of this π-nucleophile which becomes important in fast reactions.

As in previous papers dealing with the application of eq 5, it should be reminded that the rate constants predicted by eq 5 are usually accurate within a factor of 10–100 if systems with strong steric shielding (e.g., tritylium ions) or systems which are affected by anomeric effects (e.g., reactions of alkoxycarbenium ions with alcohols) are excluded. With these exceptions in mind, Figure 5 is a useful guide for designing syntheses via solvolytically generated carbocations. Synthetic investigations in the München group have shown that it is possible to base acid free Friedel–Crafts chemistry on Figure 5.[47]

Supporting Information Available: Details of the kinetic experiments, determination of the nucleophilicity parameters, as well as correlations of N_1 with N'_T, N'_{OTs}, and N_{OTs} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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