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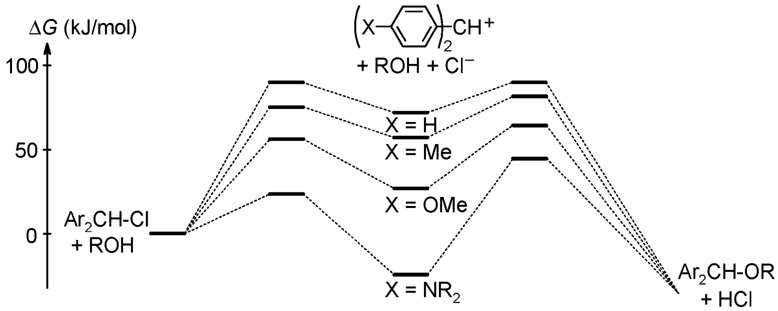

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Kinetics of the Reactions of Halide Anions with Carbocations: Quantitative Energy Profiles for S_N1 Reactions

Shinya Minegishi,† Robert Loos,† Shinjiro Kobayashi,‡ and Herbert Mayr*,†

Contribution from the Department Chemie und Biochemie der Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), D-81377 München, Germany, and IFOC, Kyushu University, Higashi-ku, Fukuoka 812-8581, Japan

Received July 23, 2004; E-mail: Herbert.Mayr@cup.uni-muenchen.de

Abstract: Rate constants for the reactions of Laser flash photolytically generated benzhydrylium ions (diarylcarbenium ions) with halide ions have been determined in various solvents, including neat and aqueous acetonitrile as well as some alcohols. Substitution of the rate constants into the correlation equation $\log k = s(N + E)$ yields the nucleophilicity parameters N for the halide ions in different solvents. Linear correlations with negative slopes are found between the nucleophilicity parameters N for Cl^- and Br^- in different solvents and the solvent ionizing powers Y of the corresponding solvents. Increasing halide solvation reduces the rates of carbocation/chloride combinations by approximately half as much as it increases the rates of ionizations of benzhydryl chlorides. Comparison of the solvent dependent nucleophilicity parameters N of halide anions and the nucleophilicity parameters N_1 for solvents yields a quantitative prediction of common ion rate depression, as demonstrated by the analysis of a variety of literature reported mass-law constants α. Combination of the rate constants for the reactions of benzhydrylium ions with halide ions (k_{-1}) reported in this work with the ionization constants of benzhydryl halides (k_1) and the recently reported rate constants for the reactions of benzhydrylium ions with solvents (k_2) yields complete quantitative free energy profiles for solvolysis reactions. The applicability of Hammond's postulate for interpreting solvolysis reactions can thus be examined quantitatively.

Introduction

Unimolecular nucleophilic substitutions (S_N1 or $D_N + A_N$, Scheme 1) are discussed in most undergraduate textbooks for introducing basic concepts of mechanistic organic chemistry, e.g., reactive intermediates, molecularity, reaction order, rate determining step, etc.

Qualitative free energy profiles, as shown in Figure 1, are usually depicted to illustrate their typical course, which involves slow ionization followed by fast trapping of the intermediate carbocation by the solvent.

Even if the differentiation of free and paired carbocations[1] is neglected, the qualitative energy profile depicted in Figure 1 cannot be generally valid. We have recently reported on the direct spectroscopic observation of the dianisylcarbenium ion during the trifluoroethanolysis of dianisylmethyl chloride, i.e., a solvolysis reaction which proceeds with fast ionization followed by slow trapping of the carbocation by the solvent (Scheme 2).[2] Obviously, this scenario, which has previously been predicted by Ingold,[3] is not in line with Figure 1. We, therefore, suggest replacing qualitative schemes as shown in Figure 1 with quantitative free energy profiles. For this purpose, knowledge of k_1, k_{-1}, and k_2, as defined in Scheme 1, is needed.

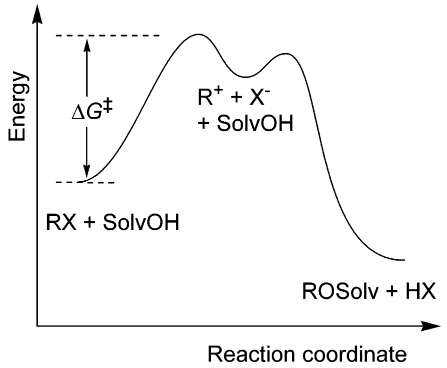

Figure 1. Typical cartoon for an S_N1 reaction as shown in most organic chemistry textbooks.

Scheme 1

$$\mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^+ + X^-} \xrightarrow[k_2]{+\ \mathrm{SolvOH}} \mathrm{ROSolv + HX}$$

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† Universität München.

‡ Kyushu University.

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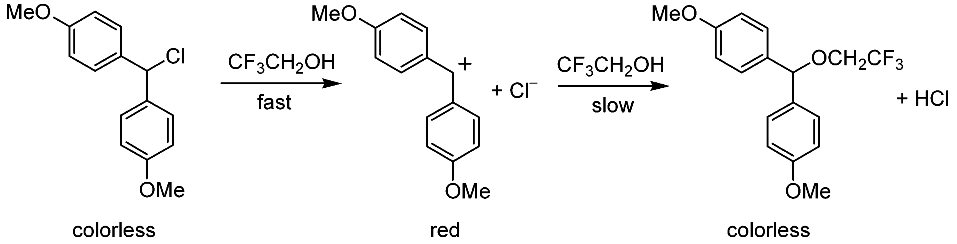
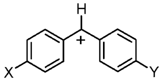
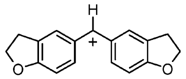
Scheme 2



Numerous kinetic investigations of solvolysis reactions of benzhydryl derivatives[4] provide the ionization constants k_1, and we have reported a correlation equation from which absolute values of k_1 for benzhydryl chlorides and bromides in frequently used solvolytic media can be derived.[5] Stopped-flow and laser flash techniques have been employed to determine absolute rate constants for the reactions of benzhydrylium ions with solvents (k_2 in Scheme 1).[5−8] Thus, the rate constants k_{-1} of Scheme 1 are the only remaining unknowns which are needed for the construction of complete free energy profiles for S_N1 solvolyses of benzhydrylium halides.

Rate constants for the reactions of some benzhydrylium ions with chloride and bromide ions (k_{-1}) in aqueous acetonitrile have previously been determined by McClelland using laser flash photolytically generated carbocations.[7b,9] In this work, we have used the same methodology for deriving quantitative relationships between structures of benzhydrylium ions and their reactivities with halide ions which will be combined with the previously reported values of k_1 and k_2 (Scheme 1) to construct quantitative energy profiles of S_N1 solvolyses. Since the stabilization of benzhydrylium ions can be modified tremendously by variation of the *para*- and *meta*-substituents, the energy profiles determined in this work can be considered to be representative also for other types of alkyl halides. We will show that energy profiles as depicted in Figure 1 can hardly ever be observed.

Scheme 3. 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
(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)$_2$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

[a] From ref 10.

Experimental Section

Materials. 2,2,2-Trifluoroethanol (TFE), methanol, and ethanol were reagent grade chemicals from commercial sources and used without further purification. Contamination of TFE by water does not harm the results because it is later shown that halide nucleophilicities are almost identical in TFE and water. 1,1,1,3,3,3-Hexafluoropropan-2-ol (reagent grade) was dried over molecular sieves 4 Å and distilled over $CaSO_4$. Commercially available acetonitrile (Wako, spectrum grade or Aldrich, H_2O < 50 ppm) was used without further purification for all laser flash experiments. For the laser flash experiments, tetra-*n*-butylammonium chloride (Fluka, ≥99% or Tokyo Kasei, >99%), bromide (Fluka, ≥99% or Tokyo Kasei, >99%), and iodide (Fluka, ≥99%) were used without further purification.

The benzhydrylium tetrafluoroborates (Scheme 3) were prepared as described in ref 10. Details will be published separately. Benzhydryl-4-cyanophenolates and benzhydryl acetates were prepared according to the procedures in ref 7.

Laser Flash Kinetics. Benzhydrylium ions were generated from 4-cyanophenolates or acetates in aqueous or alcoholic solutions in the presence of tetrabutylammonium halides. The solutions in acetonitrile used for the kinetic experiments were prepared in analogy to the published procedure for the reactions of benzhydrylium ions with the thiocyanate ion.[11]

In most cases, the decays of the benzhydrylium absorbances followed single exponentials from which pseudo-first-order rate constants ($k_{1\Psi}$) were derived. As expressed by eq 1, the pseudo-first-order rate constants $k_{1\Psi}$ include a second-order term for the reactions of the carbocations with halide ions (k_{-1} in Scheme 1) and a first-order term for the

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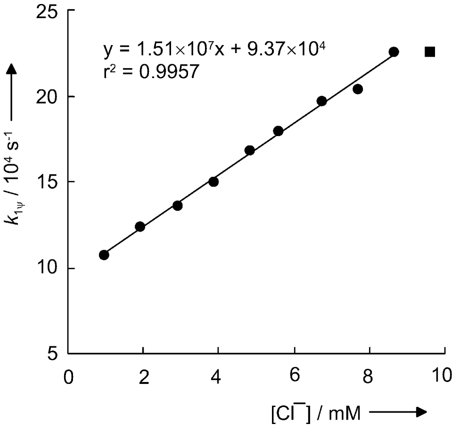

Figure 2. Linear correlation of the pseudo-first-order rate constants of the reactions of $(ani)_2CH^+$ with Cl^- in 50/50 (v/v) water/acetonitrile with the concentration of tetrabutylammonium chloride. ■ not used for the construction of the correlation line.

reactions of the carbocations with the solvents ($k_{SolvOH} = k_2$ in Scheme 1).

$$k_{1\Psi} = k_{-1}[X^-] + k_{SolvOH} \tag{1}$$

As illustrated in Figure 2, the second-order rate constants k_{-1} were obtained as the slopes of the plots of $k_{1\Psi}$ versus the concentrations of the halide anions, and the intercepts correspond to the reactions of the benzhydrylium ions with the solvent, which have independently been determined previously.[5,6]

However, the situation shown in Figure 2 is not found in all cases. Sometimes, the pseudo-first-order rate constants do not correlate linearly with the concentrations of the halide anions, and the curves are flattening at halide concentrations $[Hal^-] > (2.5-40) \times 10^{-3}$ M, probably due to the increase of ion strength. In such cases (see Supporting Information), only the linear parts of the correlations in the low concentration range were evaluated to calculate the second-order rate constants for the reactions of benzhydrylium ions with halide anions.

Sometimes the decay of the absorption did not follow a single exponential because the benzhydryl halides are partially ionic under the reaction conditions. In such cases, the carbocations are partially consumed by halide anions in fast reversible reactions, while the remaining carbocations react with the solvents in slower consecutive reactions to give alcohols or ethers (eqs 2 and 3).

$$Ar_2CH^+ + X^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Ar_2CHX \tag{2}$$

$$Ar_2CH^+ + SolvOH \overset{\text{slow}}{\rightleftharpoons} Ar_2CHOSolv + H^+ \tag{3}$$

For evaluating such kinetics, the observed decay of the absorption was fitted to a double exponential (eq 4), and eq 5 was used to obtain the rate constants for the combination of benzhydrylium ions with anions (Figure 3).

$$[A] = A_1[\exp(-r_1 t)] + A_2[\exp(-r_2 t)] \tag{4}$$

$$r_1 + r_2 = k_{-1}[X^-] + k_2 + k_1 \tag{5}$$

A derivation of eq 5, which refers to the rate constants defined in Scheme 1, is given in the Supporting Information.

According to eq 5, the slope of the correlation ($r_1 + r_2$) versus $[X^-]$ corresponds to k_{-1} (Table 1), and the intercept reflects the sum $k_2 + k_1$, as illustrated in Figure 3. Though k_2 as well as k_1 can, in principle, be derived from these intercepts ($= k_2 + k_1$) if either k_2 or k_1 is known, the precision of the rate constants thus obtained is rather low; for that reason, the intercepts of such plots have not been evaluated.

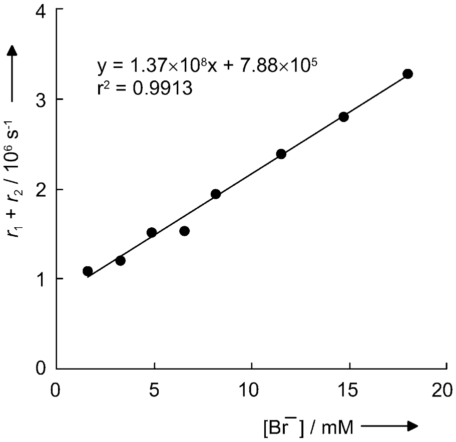

Figure 3. Linear correlation of ($r_1 + r_2$) for the reaction of $(ani)_2CH^+$ with bromide ions in 50/50 (v/v) ethanol/water.

Table 1. Kinetics of the Reactions of Halide Anions with Benzhydrylium Ions at 20 °C

Ar_2CH^+	solvent[a]	rxn with solvent k_2/s^{-1}	rxn with Cl^- $k_{-1}/M^{-1}\,s^{-1}$	rxn with Br^- $k_{-1}/M^{-1}\,s^{-1}$
$(dpa)_2CH^+$	AN		1.76×10^{7}	
$(mfa)_2CH^+$	AN		1.61×10^{8}	
$(pfa)_2CH^+$	AN		9.70×10^{8}	1.39×10^{9}
$(fur)_2CH^+$	AN		9.39×10^{9}	1.13×10^{10}
$(ani)_2CH^+$	M	8.4×10^{6}[b]	5.33×10^{7}	5.31×10^{8}
	50M50AN	2.33×10^{6}[c]	3.02×10^{8}	1.63×10^{9}
	E	5.5×10^{6}[d]	6.99×10^{8}	2.75×10^{9}
	50E50AN	1.41×10^{6}[c]	1.71×10^{9}	4.32×10^{9}
	80E20W	1.51×10^{6}[c]	6.05×10^{7}	4.84×10^{8}
	50E50W	4.96×10^{5}[c]	1.20×10^{7}	1.37×10^{8}
	80W20AN	1.0×10^{5}[b]	3.23×10^{6}	
	50W50AN	1.04×10^{5}[c]	1.51×10^{7}	1.86×10^{8}
	20W80AN	9.82×10^{4}[c]	9.53×10^{7}	7.02×10^{8}
	AN		1.5×10^{10}[f]	1.6×10^{10}[f]
$(ani)(tol)CH^+$	80E20W	7.88×10^{6}[c]	5.01×10^{8}	
	50E50W	3.86×10^{6}[c]	1.26×10^{8}	8.26×10^{8}
	W	7.8×10^{5}[g]	9.24×10^{6}[g]	8.24×10^{7}[g]
	80W20AN	8.2×10^{5}[e]	2.41×10^{7}[g]	1.53×10^{8}[g]
	50W50AN	8.55×10^{5}[c]	1.01×10^{8}	5.37×10^{8}[g]
	20W80AN	8.29×10^{5}[c]	5.29×10^{8}[g]	2.52×10^{9}[g]
	10W90AN	6.81×10^{5}[c]	2.26×10^{9}[g]	6.58×10^{9}[g]
	AN		2.44×10^{10}[g]	2.59×10^{10}[g]
$(ani)PhCH^+$	50E50W	7.91×10^{6}[c]	6.19×10^{8}	1.19×10^{9}
	W	1.90×10^{6}[g]	2.16×10^{7}[g]	2.41×10^{8}[g]
	80W20AN	1.90×10^{6}[g]	5.22×10^{7}[g]	4.37×10^{8}[g]
	50W50AN	1.84×10^{6}[c]	2.64×10^{8}	9.29×10^{8}[g]
	20W80AN	1.87×10^{6}[c]	1.02×10^{9}[g]	3.40×10^{9}[g]
	10W90AN	1.83×10^{6}[c]	3.33×10^{9}[g]	7.02×10^{9}[g]
	AN		2.20×10^{10}[g]	2.73×10^{10}[g]
	T	1.2×10^{3}[b]	2.60×10^{7}	1.92×10^{8}
$(tol)_2CH^+$	T	2.4×10^{4}[b]	2.53×10^{8}	1.76×10^{9}
$(tol)PhCH^+$	T	2.7×10^{5}[b]	1.07×10^{9}	3.89×10^{9}
	H		3.47×10^{7}	
Ph_2CH^+	T	3.2×10^{6}[b]	1.9×10^{9}[h]	6.5×10^{9}[h]
	H	5×10^{3}[i]	6.12×10^{8}	2.55×10^{9}
	AN	(2.5×10^{6})[f]	2.0×10^{10}[f]	2.1×10^{10}[f]

[a] Mixtures of solvents are given as (v/v). Solvents: M = methanol, E = ethanol, W = water, AN = acetonitrile, T = 2,2,2-trifluoroethanol, H = 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] From ref 12. [c] From ref 6. [d] From ref 13. [e] From ref 7a. [f] From ref 14. [g] From ref 7b. [h] From ref 9. [i] From ref 15.

Results and Discussion

Nucleophilicity Parameters for Halide Anions in Various Solvents. In numerous investigations we have shown that the rate constants of the reactions of carbocations with charged and noncharged nucleophiles can be expressed by

$$\log k = s(N + E) \tag{6}$$

where k is a rate constant at 20 °C in $M^{-1}\,s^{-1}$, s is a nucleophile-specific slope parameter, N is a nucleophilicity parameter, and

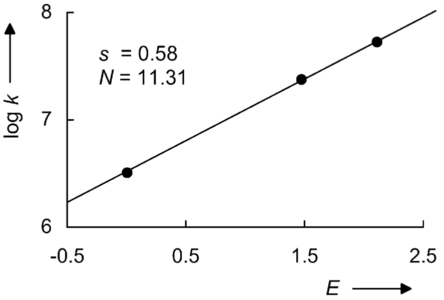

Figure 4. Plot of the rate constants for the reactions of benzhydrylium ions with chloride ions in 80/20 (v/v) water/acetonitrile versus the corresponding electrophilicity parameters E.

E is an electrophilicity parameter.[10,16–20] While this linear correlation holds well for rate constants $k < 10^8$ M^{-1} s^{-1}, the correlations log k vs E bend at higher rate constants when the diffusion limit is approached. Chloride in 80% water/20% acetonitrile (80W20AN) is the only halide anion/solvent combination listed in Table 1 for which more than two rate constants below 10^8 M^{-1} s^{-1} are available. Figure 4 shows that these rate constants correlate perfectly with the electrophilicity parameters E and give rise to the nucleophile-specific parameters $N = 11.3$ and $s = 0.58$. Closely similar values of s have been found for other anions in aqueous solution.[18,20]

Because of the paucity of suitable data ($k < 10^8$ M^{-1} s^{-1}), N parameters for other halide anion/solvent combinations have not been determined by our conventional statistical analysis of reaction series.[10] Instead, N was calculated by eq 6 from the rate constant k_{-1} of the slowest reaction investigated for the corresponding halide/solvent couple and the typical slope parameter for anions in aqueous solution ($s = 0.6$).[18,20] However, only rate constants $k_{-1} < 5 \times 10^8$ M^{-1} s^{-1} were employed for the evaluation of N. While this procedure appears arbitrary, it is justified by the excellent agreement between observed and calculated rate constants (standard deviation: factor 1.9) in Table 2.[21]

Table 2. Nucleophilicity Parameters N for Chloride and Bromide Ions in Various Solvents and Comparison between Experimental and Calculated Rate Constants (eq 6, $s = 0.6$)

anion/solvent[a]	N	Ar_2CH^+	k_{exp}/M^{-1} s^{-1}	k_{calc}/M^{-1} s^{-1}
Cl^-/M	12.9	$(ani)_2CH^+$	5.33×10^7	*b*
Cl^-/50M50AN	14.1	$(ani)_2CH^+$	3.02×10^8	*b*
Cl^-/E	14.7	$(ani)_2CH^+$	6.99×10^8	*b*
Cl^-/80E20W	13.0	$(ani)_2CH^+$	6.05×10^7	*b*
		$(ani)(tol)CH^+$	5.01×10^8	4.9×10^8
Cl^-/50E50W	11.8	$(ani)_2CH^+$	1.20×10^7	*b*
		$(ani)(tol)CH^+$	1.26×10^8	9.3×10^7
		$(ani)PhCH^+$	6.19×10^8	2.2×10^8
Cl^-/W	10.1	$(ani)(tol)CH^+$	9.24×10^{6c}	*b*
		$(ani)PhCH^+$	2.16×10^{7c}	2.1×10^7
Cl^-/80W20AN	11.3 ($s = 0.58$)[d]	$(ani)_2CH^+$	3.23×10^6	3.6×10^6
		$(ani)(tol)CH^+$	2.41×10^{7c}	2.6×10^7
		$(ani)PhCH^+$	5.22×10^{7c}	6.0×10^7
Cl^-/60W40AN	11.3	$(ani)(tol)CH^+$	4.82×10^{7c}	*b*
		$(ani)PhCH^+$	1.18×10^{8c}	1.1×10^8
Cl^-/50W50AN	12.0	$(ani)_2CH^+$	1.51×10^7	*b*
		$(ani)(tol)CH^+$	1.01×10^8	1.2×10^8
		$(ani)PhCH^+$	2.64×10^8	2.9×10^8
Cl^-/40W60AN	12.0	$(ani)(tol)CH^+$	1.27×10^{8c}	*b*
		$(ani)PhCH^+$	2.26×10^{8c}	2.9×10^8
Cl^-/20W80AN	13.3	$(ani)_2CH^+$	9.53×10^7	*b*
		$(ani)(tol)CH^+$	5.29×10^{8c}	7.4×10^8
		$(ani)PhCH^+$	1.02×10^{9c}	1.8×10^9
Cl^-/AN	17.2[e]	$(dpa)_2CH^+$	1.76×10^7	3.1×10^7
		$(mfa)_2CH^+$	1.61×10^8	1.0×10^8
		$(pfa)_2CH^+$	9.70×10^8	2.7×10^8
		$(fur)_2CH^+$	9.39×10^9	3.2×10^9
		$(ani)_2CH^+$	1.5×10^{10f}	2.1×10^{10}
Cl^-/T	10.3	$(ani)PhCH^+$	2.60×10^7	*b*
		$(tol)_2CH^+$	2.53×10^8	2.3×10^8
		$(tol)PhCH^+$	1.07×10^9	8.6×10^8
		Ph_2CH^+	1.9×10^{9g}	5.3×10^9
Cl^-/H	8.0	$(tol)PhCH^+$	3.47×10^7	*b*
		Ph_2CH^+	6.12×10^8	2.2×10^8
Br^-/80E20W	14.5	$(ani)_2CH^+$	4.84×10^8	*b*
Br^-/50E50W	13.6	$(ani)_2CH^+$	1.37×10^8	*b*
		$(ani)(tol)CH^+$	8.26×10^8	1.1×10^9
		$(ani)PhCH^+$	1.19×10^9	2.7×10^9
Br^-/W	11.7	$(ani)(tol)CH^+$	8.24×10^{7c}	*b*
		$(ani)PhCH^+$	2.41×10^{8c}	1.9×10^8
Br^-/80W20AN	12.2	$(ani)(tol)CH^+$	1.53×10^{8c}	*b*
		$(ani)PhCH^+$	4.37×10^{8c}	3.9×10^8
Br^-/60W40AN	12.8	$(ani)(tol)CH^+$	3.72×10^{8c}	*b*
		$(ani)PhCH^+$	6.15×10^{8c}	8.8×10^8
Br^-/50W50AN	13.8	$(ani)_2CH^+$	1.86×10^8	*b*
		$(ani)(tol)CH^+$	5.37×10^{8c}	1.5×10^9
		$(ani)PhCH^+$	9.29×10^{8c}	3.5×10^9
Br^-/T	11.7	$(ani)PhCH^+$	1.92×10^8	*b*
		$(tol)_2CH^+$	1.76×10^9	1.6×10^9
		$(tol)PhCH^+$	3.89×10^9	5.9×10^9
		Ph_2CH^+	6.5×10^{9g}	3.6×10^{10}

[a] Mixtures of solvents are given as (v/v). Solvents: M = methanol, E = ethanol, W = water, AN = acetonitrile, T = 2,2,2-trifluoroethanol, H = 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] $k_{calc} = k_{exp}$; value was used for the calculation of N. [c] From ref 7b. [d] From Figure 4. [e] N was calculated from rate constants of $(dpa)_2CH^+$ and $(mfa)_2CH^+$ by least-squares minimization with $s = 0.6$. [f] From ref 14. [g] From ref 9.

In agreement with the N parameters shown in Table 2, McClelland has already demonstrated the increase of the nucleophilicities of halide anions in aqueous acetonitrile mixtures with decreasing amount of water.[7b] With the N parameters now derived, we are able to compare the nucleophilicities of halide ions in different solvents with those of other nucleophiles (Figure 5).

From the N parameters for Cl^- and Br^- presented in this work and the previously published E parameter of the tritylium ion ($E = 0.51$),[18a] one can calculate rate constants for the reaction of the tritylium ion with Cl^- and Br^- in water, which are 6−20 times greater than experimentally determined by McClelland (Table 3). This deviation is within the postulated error limit (factor 10−100) of eq 6 and illustrates the power of this correlation to semiquantitatively predict the rate of any carbocation−nucleophile combination.[16]

In accord with the similar values of N for Cl^- and OH^- determined by us, McClelland observed similar rates for the

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(20) Bug, T.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 12980−12986.
(21) Of course, an even better agreement between observed and calculated rate constants in Table 2 would be achieved if a least-squares fit to eq 6 would be performed. Because of the small differences in log k, unrealistic values of s (and N) would result by this procedure, which would give rise to larger errors for rate constants outside the range investigated in this work.

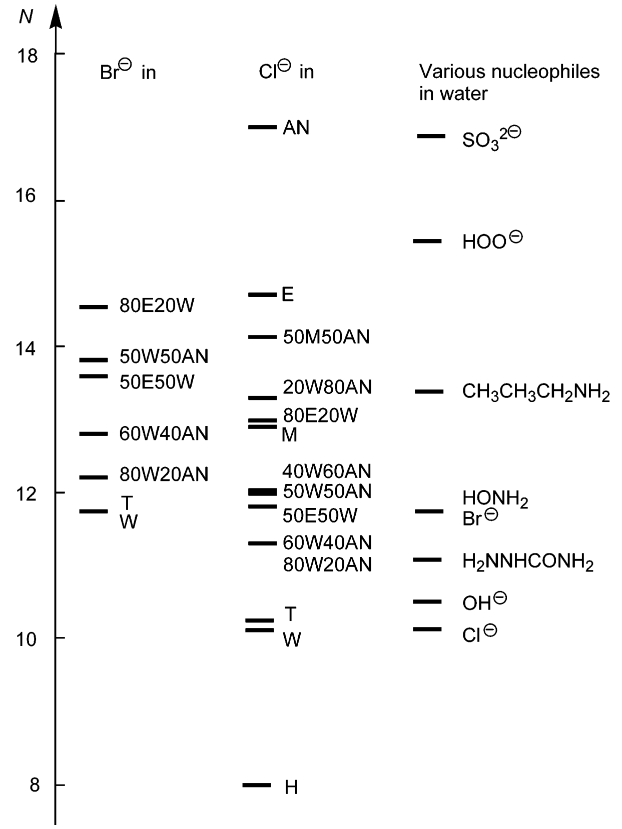

Figure 5. Comparison of the reactivities of halide anions in different solvents with those of other n-nucleophiles[18a] in water. Mixtures of solvents are given as (v/v). Solvents: M = methanol, E = ethanol, W = water, AN = acetonitrile, T = 2,2,2-trifluoroethanol, H = 1,1,1,3,3,3-hexafluoropropan-2-ol.

Table 3. Comparison of Calculated and Experimental Rate Constants ($M^{-1}s^{-1}$) for the Reaction of Cl^-, Br^-, and OH^- with the Tritylium Ion ($E = 0.51$) in Aqueous Acetonitrile

Hal^-	N/s (60W40AN)	k_{calc} (60W40AN)	k_{exp} (67W33AN)[a]
Cl^-	11.3/0.6	1.2×10^7	2.2×10^6
Br^-	12.8/0.6	9.7×10^7	5×10^{6b}
OH^-	10.19/0.62[c]	4.3×10^6	5.2×10^6

[a] From ref 22. [b] $[Br^-] = 0.1-0.3$ M (KBr). [c] N and s for 50W50AN from ref 18a.

reactions of the tritylium ion with Cl^- and OH^- in aqueous acetonitrile (Table 3).[22] In contrast, Richard derived $N_+ = 1.2$ for Cl^- in water,[23] which implies that Cl^- is 3.5 orders of magnitude less reactive than OH^- ($N_+ = 4.75$).[24] The reason for this discrepancy is presently not clear.

Relationship between Halide Nucleophilicities and Solvent Ionizing Power. The strong dependence of halide nucleophilicities on solvent can be explained by halide solvation, mostly by hydrogen bonding, which is abandoned during formation of the covalent adduct. Since the combinations of carbocations with halides studied in this work (k_{-1}, Scheme 1) are the reverse of the ionization step in solvolysis reactions (k_1, Scheme 1), the N parameters of Cl^- and Br^- in different solvents should be related to the solvent ionizing power Y.

This is indeed the case: Figure 6 shows that the nucleophilicity of chloride in ethanol exceeds that in hexafluoropropan-2-ol by almost 7 units in N. At the same time, the solvent ionizing power Y_{Cl} of ethanol is 7 units smaller than that of hexafluoropropanol-2-ol.[25] If one substitutes $N(Cl^-)$ by $(\log k_{-1})/0.6 + \text{const}$ (from eq 6 and Table 2) and Y_{Cl} by $(\log k_1)/0.9 + \text{const}'$ (from ref 26) into the correlation equation for Figure 6, one arrives at $\log k_{-1} = -0.5 \log k_1 + \text{const}''$ which implies that the solvent effect on the cation−chloride combination is half as strong as on the corresponding ionization reaction, in line with ion-like transition states.

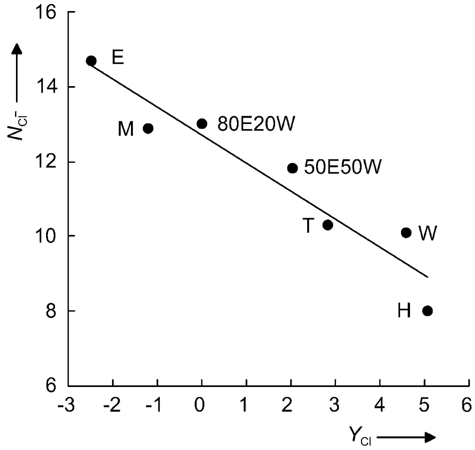

Figure 6. Correlation of N parameters of Cl^- in several solvents with the solvent ionizing power Y_{Cl} (derived from 1-adamantyl chloride solvolysis) of the corresponding solvents.[25] $N_{Cl^-} = -0.75Y_{Cl} + 12.7$, $n = 7$, $r^2 = 0.916$.

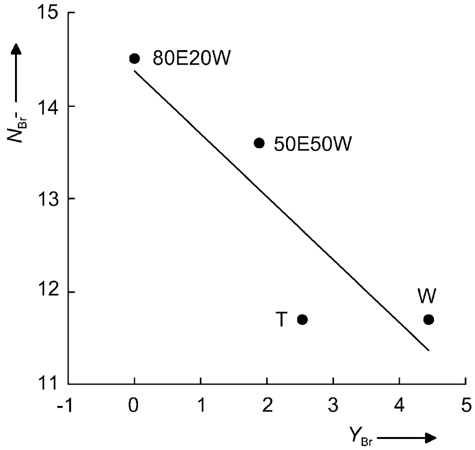

Figure 7. Correlation of N parameters of Br^- in several solvents with solvent ionizing power Y_{Br} (derived from 1-adamantyl bromide solvolysis) of the corresponding solvents.[25] $N_{Br^-} = -0.68Y_{Br} + 14.4$, $n = 4$, $r^2 = 0.781$.

A correlation of comparable slope (Figure 7) was found between N for bromide in different solvents and Y_{Br},[25] but because of the paucity of data, this correlation is less meaningful. More correlations between N and various Y-scales, all with similar slopes, are shown in the Supporting Information.

Common Ion Rate Depression. According to the solvolysis scheme by Hughes and Ingold[27] (Scheme 1), the intermediate carbocation R^+ can either react with the solvent to yield the product or with the halide ion to regenerate the alkyl halide RX. Using the steady-state approximation and neglecting the

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(27) See p 483 in ref 3.

effects of variable ionic strength, the observed solvolysis rate constants can be expressed by eq 7.

$$k_{\text{obs}} = \frac{k_1 k_2}{k_2 + k_{-1}[\text{X}^-]} = \frac{k_1}{1 + \alpha[\text{X}^-]} \qquad (7)$$

The mass-law constant $\alpha = k_{-1}/k_2$ has the dimension M^{-1} and reflects the relative reactivities of X^- and solvent toward the carbocation; it is often extrapolated to zero ionic strength ($\alpha° = k_1^{\circ}/k_2$).[3] A reduction of k_{obs} by addition of a salt with a common anion X^-, as expressed by eq 7, can only be observed when the carbocation is sufficiently selective to react competitively with the more nucleophilic X^- that is present in low concentration and with the less nucleophilic solvent that is present in high concentration. Ingold has already recognized that this is the case for benzhydryl halide solvolysis in aqueous acetone but not for *tert*-alkyl halides under the same conditions.[3] It has been shown that α increases with increasing stabilization of the carbocations and decreasing nucleophilicity of the solvents.[28]

We can now employ Figure 8 which is based on the data in Table 1 and in ref 6 to quantitatively derive the magnitudes of the mass-law constants, because the differences between the correlation lines for halides and solvents equal log α°.

Figure 8a, for example, shows that, in 20W80AN, the mass law constant α° decreases from 10^3 for $(\text{ani})_2\text{CHCl}$ ($E = 0$) to ≈ 10 for Ph_2CHCl ($E = 5.9$), in agreement with α-values reported for benzhydryl chloride solvolyses in 15% to 30% aqueous acetone in the literature (Table 4, entries 1−8). As expected from Figure 8a, the solvolysis of *tert*-butyl bromide ($E = 8.5{-}9$)[37] in aqueous acetonitrile (or acetone) does not show common ion rate depression (Table 4, entry 9).

Common ion rate depression can be expected to be much greater in trifluoroethanol, a solvent with low nucleophilicity ($N_1 = 1.23$, $s = 0.92$).[6] Whereas the chloride and 20W80AN correlation lines are close to meeting at $E = 6$ (Figure 8a), the chloride and TFE correlation lines are still far apart from each other at $E = 6$ and only meet at $E \approx 10$ (Figure 8b). This is in line with the reported α-values for solvolyses of bis(*p*-chloro)benzhydryl chloride [$(\text{pcp})_2\text{CHCl}$, $E = 6.02$][10] in ethanol/trifluoroethanol mixtures[34] (Table 4, entries 10−13). While we do not know the solvent nucleophilicities of ethanol/trifluoroethanol mixtures, nucleophilicity parameters for aqueous trifluoroethanol and for pure trifluoroethanol ($N_1 = 1.23$) have been determined.[6] If one assumes 80T20E to resemble 80T20W ($N_1 = 3.20$),[6] the corresponding correlation line can be expected to be two units above that of trifluoroethanol in Figure 8b. Since, at the same time, only a slight increase of chloride nucleophilicity (compared to Cl^- in TFE) can be expected, the observed value of $\alpha = 41$ for a carbocation with $E = 6.02$ (Table 4, entry 10)[34] is in line with Figure 8b. When TFE is gradually exchanged by ethanol, halide and solvent correlation lines get closer to each other and the reported decrease in α (Table 4, entries 11−13) is in qualitative agreement with this analysis.

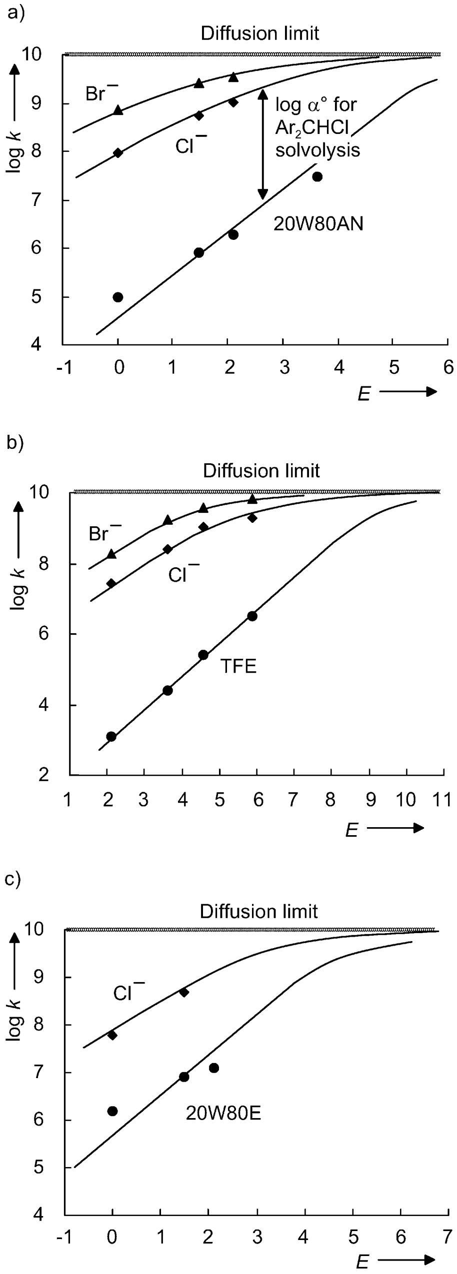

Figure 8. Comparison of the second-order rate constants of the reactions of benzhydrylium ions (characterized by their electrophilicities *E*, from ref 10) with Cl^- and Br^- in (a) 80% aqueous acetonitrile (20W80AN), (b) trifluoroethanol (TFE), and (c) 80% aqueous ethanol (20W80E) with the first-order rate constants for the reactions of the benzhydrylium ions with the same solvents. The correlation lines for the reactions with solvents are based on more rate constants which are outside the range shown in Figure 8.

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(30) Calculated from $N_1 = 1.23$ and $s = 0.92$ for trifluoroethanol (from ref 6) and the rate constant of $2.3 \times 10^5\ \text{s}^{-1}$ for the reaction of the 1-(*p*-anisyl)-2,2-dimethyl vinyl cation with trifluoroethanol determined by: Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1999**, *77*, 2069−2082.

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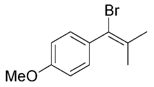
Table 4. Mass-Law Constants α Reported for the Solvolyses of Various Alkyl Chlorides and Bromides

entry	Substrate R-X	$E(R^+)$ [a]	Solvent [b]	T / °C	α	Ref.
1	$(ani)_2CH\text{-}Cl$	0	15W85A	0	3700	31
2	(ani)(tol)CH-Cl	1.48	15W85A	0	1500	31
3	(ani)PhCH-Cl	2.11	15W85A	0	700	31
4	(pop)PhCH-Cl	2.90	15W85A	0	140	31
5	$(tol)_2CH\text{-}Cl$	3.63	20W80A	0	74	32
6	(tol)PhCH-Cl	4.59	20W80A	25	32	32
7	$Ph_2CH\text{-}Cl$	5.90	20W80A	25	11.5	32
			30W70A	0	2.08	31
8	$(4\text{-}NO_2C_6H_4)PhCH\text{-}Cl$	≈ 9 [c]	30W70A	0	0.71	31
9	$(CH_3)_3C\text{-}Br$	8.5–9 [d]	10W90A	25	≈ 1	33
10	$(pcp)_2CH\text{-}Cl$	6.02	80T20E	0	41	34
11			70T30E	25	10	34
12			50T50E	25	6	34
13			30T70E	25	4	34
14		4.6 [e]	20W80E	120	very small	35
15			T	35	394	36

[a] Electrophilicity parameters E from ref 10 unless noted otherwise. [b] Mixtures of solvents are given as (v/v). Solvents: A = acetone, E = ethanol, W = water, T = trifluoroethanol. [c] From ref 5. [d] From ref 37. [e] From ref 30.

Because of the high intrinsic barriers for the reactions of vinyl cations with nucleophiles, vinyl cations are less electrophilic than expected from their solvolyses rates.[29] For the 1-(*p*-anisyl)-2,2-dimethylvinyl cation, an electrophilicity parameter of $E = 4.6$ can be derived from the rate of its reaction with trifluoroethanol (laser flash experiment).[30] Figure 8c shows that a carbocation of this electrophilicity can be expected to possess little selectivity in 80% aqueous ethanol (20W80E), but Figure 8b indicates high selectivity in trifluoroethanol in line with entries 14 and 15 in Table 4.

Though the presently available E and N parameters do not exactly mirror the conditions of the corresponding experiments in the literature, it is obvious that a semiquantitative prediction of common ion effects has become possible.

Construction of Energy Profiles for S_N1 Solvolyses. The rate constants for the reactions of halide ions with benzhydrylium ions determined in this work can now be combined with the ionization rate constants of benzhydrylium halides[5] and the rate constants for the reactions of benzhydrylium ions with solvents[6] to construct free energy profiles for the solvolysis reactions of benzhydryl chlorides and bromides.

In previous work, we have reported that the ionization constants k_1 of benzhydryl derivatives can be expressed as a function of the nucleofuge-specific parameters s_f and N_f and the electrofuge specific parameter E_f (eq 8).[5] While E_f refers to a certain carbocation, s_f and N_f refer to a combination of leaving group and solvent.

Ionization constant:

$$\log k_1\ (25\ °C) = s_f\,(N_f + E_f) \qquad (8)$$

Rate constants, which are either directly measured or calculated by the correlation eqs 6 and 8,[5,10] are converted into activation free enthalpies by the Eyring equation.

Figure 9 shows that ionization of benzhydryl chloride (X = H) in 80% aqueous ethanol yields the parent benzhydrylium ion, which undergoes diffusion-controlled reactions with chloride ions as well as with the solvent. When the benzhydrylium ion is stabilized by two 4-CH_3 groups, its reaction with chloride remains diffusion controlled, but the rate of the reaction with the solvent is getting below diffusion control ($k_2 \approx 10^8\ s^{-1}$). In both cases, the carbocation is in a shallow energy minimum, and the approximation (Hammond postulate) that the transition state of the ionization reaction has a similar energy as the intermediate carbocation is thus experimentally proven. In contrast, the ionization of dianisylmethyl chloride (X = OCH_3) in 80% aqueous ethanol [$\tau_{1/2}$(ionization) = 3.3×10^{-4} s] yields a carbocation which meets significant barriers in the reactions with the solvent as well as with chloride ions. Both reactions are faster, however, than the ionization which implies that the concentration of the carbocation will be low throughout the reaction. The bis-*N*-morpholino-substituted benzhydryl chloride [$(mor)_2CHCl$] does not exist as a covalent species in aqueous ethanol. Figure 9 shows that, in a 1 M solution of $R_4N^+Cl^-$ in 80% aqueous ethanol, the corresponding benzhydrylium tetrafluoroborate (X = *N*-morpholino) will react faster with Cl^- than with solvent. Because of unfavorable thermodynamics, only a small equilibrium concentration of covalent $(mor)_2CHCl$ will be produced, however, before the irreversible reaction with the solvent takes place.

The fact that the barrier for ion combinations is generally smaller than the barrier for the reaction of a carbocation with the solvent does not contradict the observation that in S_N1

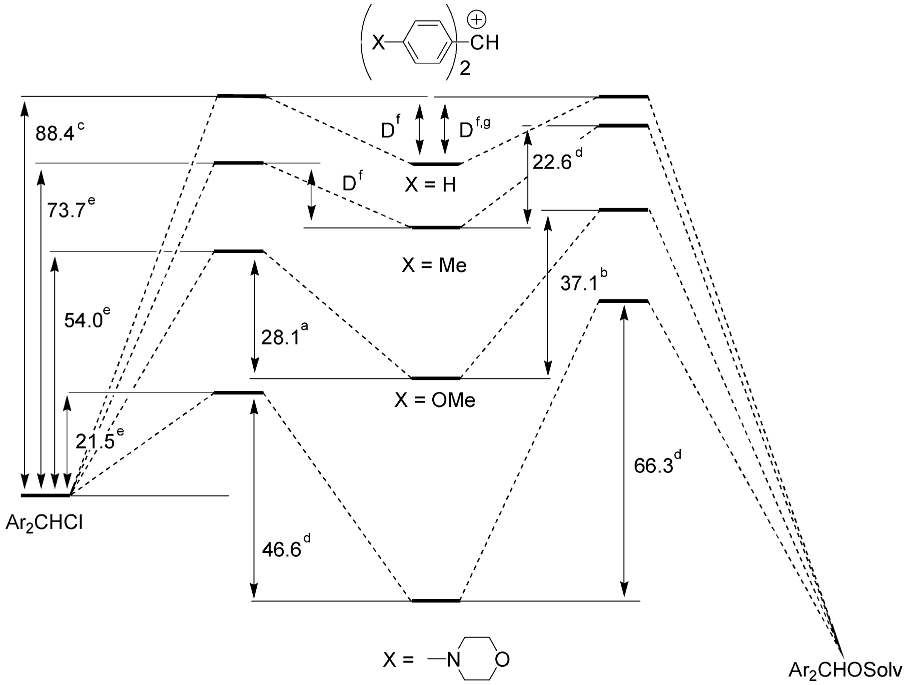


Figure 9. Free energy profiles (kJ mol^{-1}) for the solvolysis of benzhydryl chlorides in 80% aqueous ethanol at 20 °C (25 °C for k_1). [a]Direct measurement, Table 1. [b]Direct measurement, ref 6. [c]Direct measurement, ref 5. [d]Calculated by eq 6 using data in Table 2 and ref 6. [e]Calculated by eq 8 and data from ref 5. For (mor)$_2$CH$^+$ E_f was estimated from the correlation $E_f = -1.03E + 0.05$ (ref 5). [f]Diffusion-controlled rate constants of $3 \times 10^9 - 3 \times 10^{11}$ M^{-1} s^{-1} (ref 8a) correspond to $\Delta G^{\ddagger} = 7.4-18.6$ kJ mol^{-1} at 20 °C. [g]Direct measurement in 100% ethanol: $k = 1.4 \times 10^{10}$ s^{-1} (ref 38).

reactions the ionization step is often rate-determining when the concentration of halide ions in the solution is small.

From the solvolysis rate constant of *tert*-butyl chloride in 80% aqueous ethanol (9.26×10^{-6} s^{-1} at 25 °C),[39] one can calculate $\Delta G^{\ddagger} = 102$ kJ mol^{-1} for the ionization step, i.e., a value somewhat higher than that for the parent benzhydrylium ion. Since Scheme 9 in ref 16b shows that other types of sp^2-hybridized carbocations also follow linear correlations between E and the corresponding solvolysis rate constants, one can conclude that the relationships derived for benzhydrylium ions in this work hold analogously for such systems.

The corresponding energy profiles in 2,2,2-trifluoroethanol (Figure 10) differ significantly from those in 80% aqueous ethanol. Due to the better solvation of Cl$^-$ by CF$_3$CH$_2$OH than by 80% aqueous ethanol, the barriers for ionization are generally lower and the barriers for the carbocation−chloride combination are higher than those in aqueous ethanol. As the solvent nucleophilicity of CF$_3$CH$_2$OH ($N_1 = 1.23$) is lower than that of 80% aqueous ethanol ($N_1 = 6.68$),[6] also the barriers for the combination with the solvent are higher in Figure 10 than in Figure 9. As a consequence, the carbocationic intermediates are generally surrounded by higher barriers in trifluoroethanol than in aqueous ethanol. Because (ani)$_2$CH$^+$ + Cl$^-$ is only 2 kJ mol^{-1} higher in standard free energy than its covalent counterpart (ani)$_2$CHCl (Figure 10), dissolution of a 10^{-5} M solution of (ani)$_2$CHCl in trifluoroethanol led to almost quantitative ionization, and the intermediate carbocation could be observed spectroscopically before it reacted with the solvent in a slower consecutive reaction.[2] Only 65% of (ani)$_2$CHCl was instantaneously ionized, however, when it was dissolved in a solution of 10^{-2} M tetra-*n*-butylammonium chloride in trifluoroethanol,[2] in agreement with Figure 10, which indicates comparable standard free energies of covalent and ionic dianisylmethyl chloride in trifluoroethanol.

In an analogous manner, further rate constants k_1 and k_2 (listed in refs 5 and 6) and k_{-1} values from Table 2 in this work can be combined to construct energy profiles for solvolyses of benzhydryl chlorides and bromides in other solvents.

We now can turn to the question to which extent do rates of solvolysis reactions reflect the relative energies of the carbocations. Usually, carbocations are considered as high-energy intermediates, and Hammond's postulate[42] has been employed to justify that the transition states leading to reactive intermediates are close to the latter in energy. In a more sophisticated approach, Arnett, Petro, and Schleyer demonstrated that the free energies of activation for the solvolysis of alkyl chlorides in ethanol correlate with the heats of ionization of the same alkyl chlorides in superacid solution.[43] From the slope of the correlation line (0.89), it was concluded that "carbocation character" is largely developed in the solvolysis transition states. We can now approach this problem more directly.

Figure 9 shows that in 80% aqueous ethanol, carbocations with $E > 3$ (see Scheme 3) will undergo diffusion-controlled reactions with chloride and with the solvent, which implies that the solvolysis transition states fully reflect the relative energies of the carbocations being generated. Since carbocations with $E = 3$ are generated with a half-life of 0.3 s at 25 °C,[44] one can

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(44) By using eq 8, $E \approx -E_f$, and $N_f = 3.36$ and $s_f = 0.99$ for Cl$^-$ in 80% aqueous ethanol (from ref 5), an ionization rate of $k_1 = 2.27$ s^{-1} is calculated.

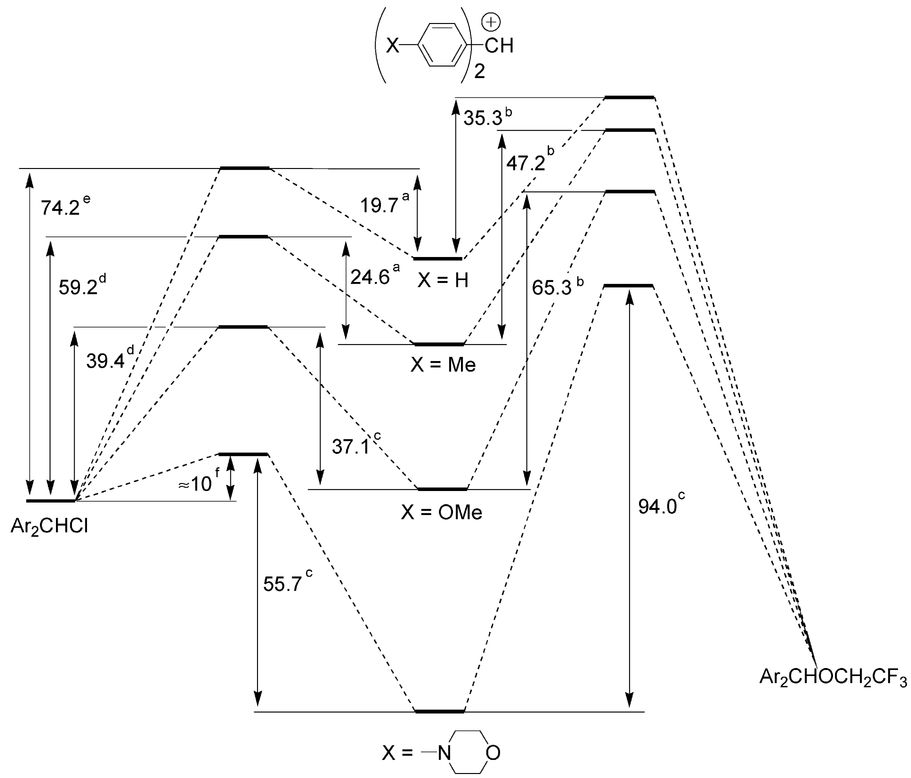

Figure 10. Free energy profiles (kJ mol^{-1}) for the solvolysis of various benzhydryl chlorides in trifluoroethanol (TFE) at 20 °C (25 °C for k_1). [a]Direct measurement, Table 1. [b]Direct measurement, ref 12. [c]Calculated by eq 6 using data in Table 2 and ref 6. [d]Calculated by eq 8 and data from ref 5. N_f for Cl$^-$ in TFE was calculated by eq 8 to 5.9 from the rate constant of Ph_2CHCl in TFE (6.17×10^{-1} s^{-1})[40] assuming $s_f = 1$. [e]Direct measurement, ref 40. [f]For $(mor)_2CH^+$ E_f was calculated from the correlation $E_f = -1.03E + 0.05$ (ref 5). Substitution of E_f for $(mor)_2CH^+$ into eq 8 predicts a rate constant > 10^{11} s^{-1}. We therefore assumed the rate constant of 1×10^{11} s^{-1} for solvent reorganization (from ref 41).

conclude that this situation is encountered in all solvolysis reactions in aqueous ethanol which have solvolysis half-lives of more than a second. An exception to this rule are vinyl halides which ionize via high intrinsic barriers and, therefore, do not follow the approximation $E_f \approx -E$ (ref 5). Furthermore, deviations may be expected for acceptor-substituted carbocations which also react via untypically high intrinsic barriers.[45]

Figure 10 shows, however, that this situation is different in trifluoroethanolysis: Because of the higher barriers for carbocation chloride combinations, the activated complex of the ionization reaction is higher in energy than the corresponding carbocation. Since there are, furthermore, significant barriers for the reactions of many carbocations with CF_3CH_2OH, one has to conclude that the observed activation energies for solvolysis in fluorinated alcohols often are considerably higher than the standard free energies of the intermediate carbocations.

Conclusion

With the halide nucleophilicities determined in this work, it has become possible to construct complete free energy profiles for S_N1 reactions which allow one to rationalize a large variety of phenomena in solvolysis reactions on the basis of absolute rate constants, which can be expressed by correlation equations. Though this work is restricted to benzhydryl derivatives which permit unequivocal interpretations because of the constancy of steric effects, its implications are more general. We have previously shown that eq 6 does hold not only for combinations of benzhydrylium ions with nucleophiles but also for other types of carbocations, though with lower accuracy.[16] Since the same is true for eq 8, a systematic ordering of a large variety of experimental observations becomes possible. By using less stabilized benzhydrylium ions, it should be possible also to describe the change from S_N1 to S_N2 reactions on the basis of absolute rate constants along the lines previously shown by Richard and Jencks.[46]

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Supporting Information Available: Details of the kinetic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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