

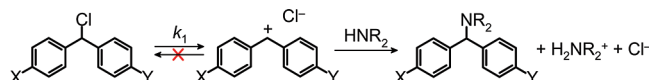
Suppression of Common-Ion Return by Amines: A Method to Measure Rates of Fast S_N1 Reactions

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Rate constants for solvolyses of benzhydryl chlorides, which take place on the 10 ms to minute time scale, have been determined in aqueous acetone and acetonitrile by conductometry, using conventional conductometers as well as stopped-flow techniques. Secondary and tertiary amines were used to suppress ion recombination (common-ion return) thus giving access to the ionization rate constants k_1 . The observed common-ion rate depressions can be rationalized by the correlation equation for electrophile–nucleophile combinations, $\log k(20\text{ }^\circ\text{C}) = s(E + N)$, where electrophiles (here: carbocations) are characterized by the parameter E and nucleophiles (here: chloride anions and solvents) are characterized by N and s .

Introduction

Rates of S_N1 reactions have been the major source of information on the stabilities of carbocations.¹ If the carbocation R⁺ is a short-lived, high-energy intermediate, the transition state of the ionization process (k_1) can be approximated by the structure and energy of the carbocation. This hypothesis, previously based on Hammond's postulate,² has been examined by the determination of the rate constants of

the reactions of the carbocations R⁺ with the leaving groups X[−] and the solvents HOSolv.^{3–5} Many of these reactions have been found to be diffusionally limited and to proceed without activation energy. In these cases, the principle of microscopic reversibility requires that there is also no barrier for the forward reaction (RX → R⁺ + X[−]), i.e., the activation free energy of the ionization step (k_1) equals the difference between the free energy of the ion pair (R⁺X[−]) and its precursor (R–X) (Figure 1A).

Figure 1D illustrates the other extreme, i.e., the heterolytic cleavage of a substrate that yields a persistent carbocation. In this case, the kinetics of the heterolysis reaction have been measured directly by monitoring the concentration of the colored carbocations.⁶ In line with noncarbocation-like transition states, in such reactions the correlation between the rates of heterolysis and the “stabilities” of the carbocations (derived from the ionization equilibria) is rather poor. The same is true for S_N2C⁺ reactions, where carbocations are formed as long-lived, directly observable intermediates, before they undergo subsequent reactions with the solvent (Figure 1C).⁷

In the course of our efforts to develop a comprehensive scheme of heterolysis reactions ranging from classical S_N1 mechanisms on one end (Figure 1A) over the S_N2C⁺

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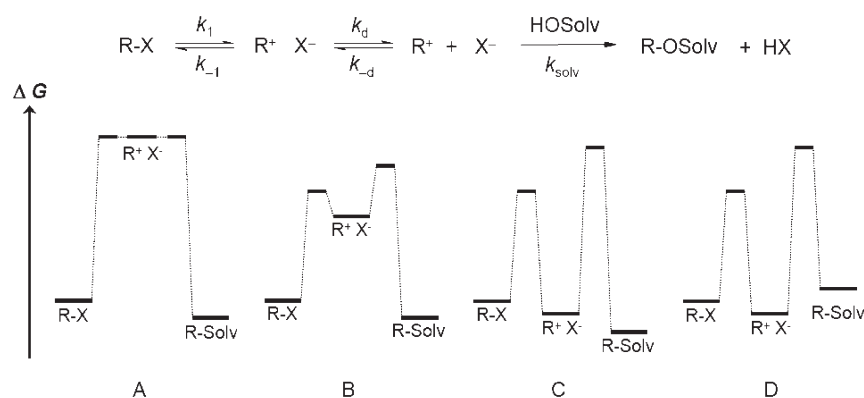


FIGURE 1. Qualitative free energy profiles for different types of solvolysis reactions.

mechanisms^{7,8,9a} (Figure 1C) to cases where persistent carbocations are generated which do not undergo subsequent reactions with the solvent (Figure 1D),⁶ we have now investigated S_N1 reactions, which proceed via carbocations of intermediate reactivity (Figure 1B). These are typically fast reaction sequences, where the first step is reversible because the intermediate carbocation reacts faster with the leaving group than with the solvent. As the overall solvolysis rate constants of such reactions are retarded by the so-called common-ion return,^{10,11} the rate of the ionization step (k_1) can only be measured directly when the recombination of the carbocation R⁺ with the leaving group X⁻ is suppressed. In this article, we will demonstrate that this can efficiently be achieved by the addition of amines. Because under these conditions ionic products are generated from covalent substrates, the rates of the reactions can be followed by conductometry. When common-ion return is suppressed in the usual way by azide ions,^{10a} the total number of ions remains constant during the reactions, and conductometry is not applicable. In this article we will demonstrate that conductometric studies of solvolysis reactions in the presence of amines are an efficient method to systematically study ionization rates of substrates which solvolyze in the millisecond to minute time scale for which only very few kinetic data are available in the literature.¹

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TABLE 1. Benzhydryl Chlorides 1a–j and Electrophilicity Parameters E^{σ} of the Corresponding Benzhydrylium Ions 1a⁺–j⁺

	X	Y	E^{σ}
1a	Cl	Cl	6.02
1b	H	H	5.90
1c	Me	H	4.59
1d	Me	Me	3.63
1e	OMe	H	2.11
1f	OMe	Me	1.48
1g	OMe	OPh	0.61
1h	OMe	OMe	0.00
1i			-0.56 ^b
1j			-1.36

^aFrom ref 12. ^bUnpublished.

Results

Solvolyses of the benzhydryl chlorides 1a–j (Table 1) in aqueous acetone or aqueous acetonitrile give rise to the formation of benzhydrols and equimolar amounts of HCl. By portionwise addition of a rapidly solvolyzing benzhydryl chloride (1g) and determination of the conductivity after completion of the solvolysis (a few seconds after each addition), the calibration curve of Figure 2 was obtained, which showed that the conductivity is directly proportional to the amount of solvolyzed benzhydryl chloride.

When the solvolyses were carried out in the presence of amines, benzhydrols and/or benzhydrylammonium salts are formed (Scheme 1). Calibration experiments as depicted in Figure 2 are reported in Figures S1 and S2 of the Supporting

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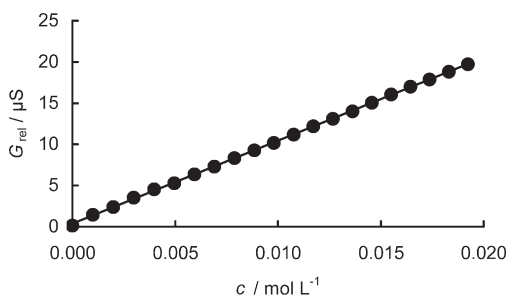
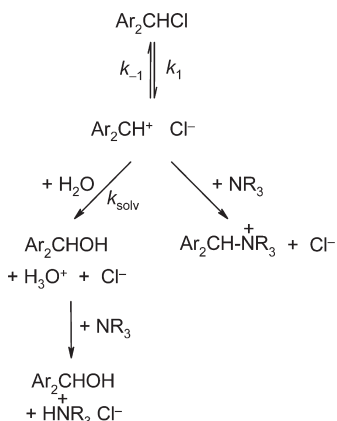


FIGURE 2. Plot of conductivity G_{rel} versus concentration of the solvolyzed substrate 4-methoxy-4'-phenoxybenzhydryl chloride **1g** without additives in 80% acetone (80A20W).

SCHEME 1. Solvolyses of Benzhydryl Chlorides in the Presence of Tertiary Amines in Aqueous Solvents



Information, which show that also under these conditions the concentration of the ions is directly proportional to the measured conductivity.

A typical example for the determination of the ionization rate constants is illustrated in Figure 3 for the solvolysis of 4,4'-dimethoxybenzhydryl chloride **1h** in 90% acetone (90A10W).

When **1h** (0.018 M) was dissolved in 90% acetone without any additives, 90% conversion was reached after 5 s, and the plot of conductivity versus time deviated noticeably from the monoexponential function (eq 1), which is shown by the dashed line in Figure 3a.

$$G = G_{\text{max}}[1 - \exp(-k_1 t)] + \text{constant} \quad (1)$$

When the reaction was followed in a solution containing 0.04 M piperidine, 90% conversion was already achieved after 0.2 s, and the experimental line got closer to the dashed exponential function (Figure 3b). Accordance between the experimental graph and the exponential function was found when 0.24 M piperidine was present, and 90% of conversion was now achieved after 0.1 s (Figure 3c).

Because the rate laws to describe the kinetics in panels a and b of Figure 3 are rather complex (concentrations of Cl^- vary during the reactions) we did not attempt to describe these traces in detail. We rather extracted “first-order rate constants” k_{obs} from best fits of these graphs to the exponential function (eq 1). Though these values of k_{obs} are not well-defined, they give useful information on the half-lives of the substrates under the given reaction conditions.

When quoted in the tables, these concentration-dependent “rate constants” are displayed in italics, whereas in the figures they are represented by open symbols.

Figure 3d shows that the rate of the reaction increased significantly upon addition of small concentrations of piperidine, but decreased slightly as the piperidine concentration exceeds 0.24 M. Because ionization of the C–Cl bond requires solvation of the incipient chloride ion by hydrogen bonding, one might explain the decrease of reactivity at high amine concentrations by a solvent effect: The water molecules which are needed for chloride solvation are no longer fully available because they are already engaged in hydrogen bonding with the amine. An alternative explanation would be the change of the dielectric constant of the solvent when higher concentrations of amine are present.

A similar behavior was observed when the solvolysis of 4,4'-dimethoxybenzhydryl chloride **1h** was carried out in the presence of variable concentrations of triethylamine, 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO), and pyridine as depicted in Figure 4, where the slight reactivity decrease at higher amine concentrations, which is shown in the Supporting Information, has been cut off for the sake of clarity. Addition of the sterically shielded 2,6-lutidine (= 2,6-dimethylpyridine), which is a stronger Brønsted base than pyridine, does not affect the kinetics of the solvolysis reactions. This observation indicates that the amine effect is due to nucleophilic attack of the amine at the benzhydrylium system and not due to Brønsted base catalysis.

In accord with this interpretation, the solvolysis of 4,4'-dimethoxybenzhydryl chloride **1h** in 90% acetone (90A10W) in the presence of 0.25 M piperidine leads to the exclusive formation of the benzhydrylpiperidine **3** (Scheme 2). The benzhydrylammonium ions **2** obtained from **1h** and tertiary amines were not stable under the reaction conditions and hydrolyzed to give the corresponding benzhydrol **4**. However, because the ammonium chlorides **2** and $\text{HNR}_3^+\text{Cl}^-$ cannot be expected to have identical equivalent conductivities, the observation of monoexponential rate laws at high amine concentrations indicates that the hydrolyses of the intermediate ammonium ions **2** occur after the complete consumption of **1h**.

The observation that the solvolysis rate constants k_{obs} reach plateaus when the amine concentrations exceed a certain value (Figures 3d and 4) excludes the operation of $\text{S}_{\text{N}}2$ mechanisms. It indicates that the acceleration of the gross reactions by amines is due to the suppression of common-ion return, i.e., suppression of the reversibility of the first step of Scheme 2.

This interpretation is in line with the reactivities of 4-methoxybenzhydryl chloride (**1e**) studied under different conditions in 60% acetone (60A40W). The solvolysis of a 1 mM solution of **1e** follows first-order kinetics with a rate constant of 18.4 s^{-1} (at $c(\text{DMAP}) = 0 \text{ mol L}^{-1}$) (Figure 5). Because of the low concentration of the substrate, recombination of the intermediate carbenium ion 1e^+ with Cl^- ($c < 1 \text{ mM}$) does not efficiently compete with the trapping by water.

In an 8 mM solution of **1e**, the growing concentration of Cl^- during the reaction is responsible for the gradual retardation of the overall reaction as the common-ion return increases during the reaction. The “best fit” to the exponential function yields a value of k_{obs} that is approximately 25%

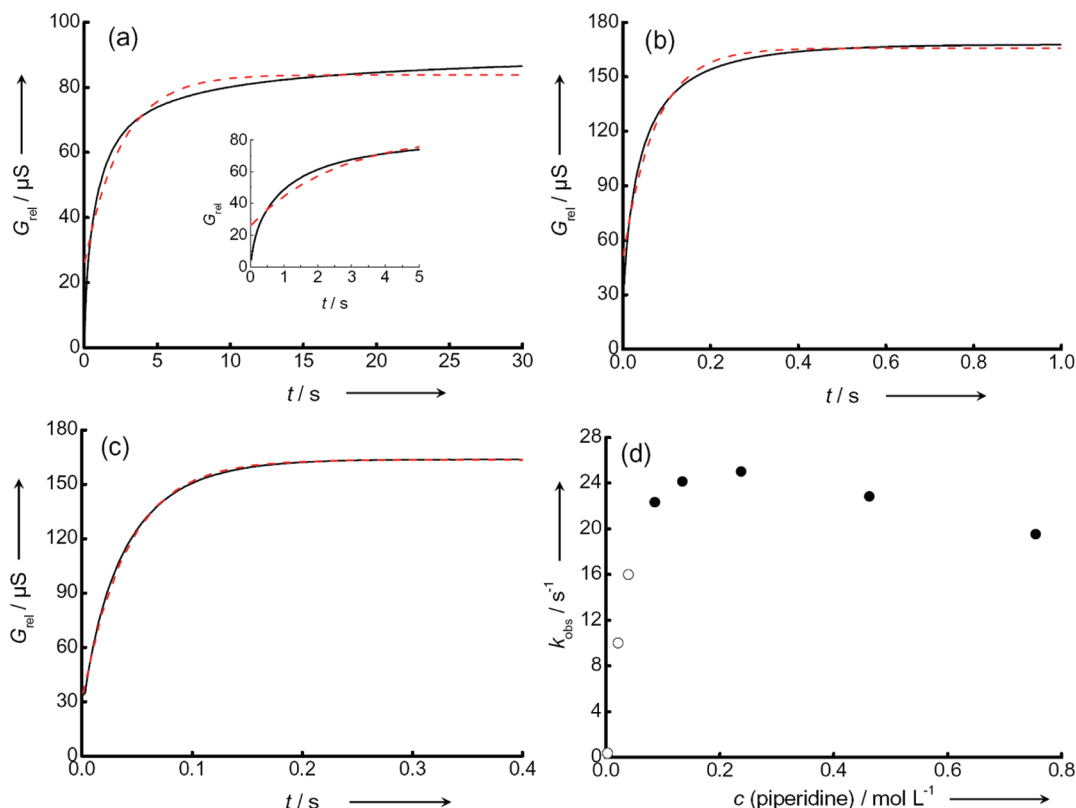


FIGURE 3. (a–c) Plots of conductivity versus time for the solvolysis of 4,4'-dimethoxybenzhydryl chloride **1h** (0.018 M) in 90% acetone (90A10W) at 25 °C in the presence of $c(\text{piperidine}) = 0$ (a), 0.04 (b), and 0.24 mol L⁻¹ (c); (d) plot of the observed rate constants k_{obs} versus $c(\text{piperidine})$ (open symbols represent kinetics that are not of first-order).

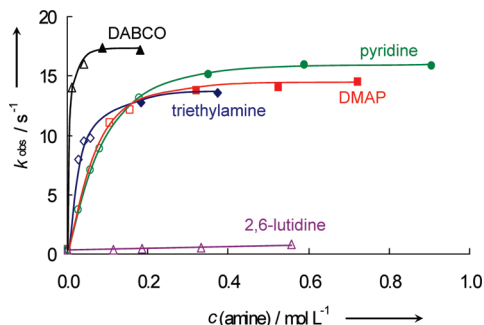


FIGURE 4. Observed rate constants of the solvolysis of 4,4'-dimethoxybenzhydryl chloride **1h** in 90% acetone (90A10W) in the presence of variable concentrations of amines (open symbols represent kinetics that are not of first-order).

smaller than that of the 1 mM solution in the absence of an amine. The kinetics of the solvolysis reaction of an even more concentrated solution of **1e** ($[\mathbf{1e}]_0 = 18 \text{ mM}$, $[\text{DMAP}] = 0$) showed a stronger deviation from the exponential function and a further significant decrease of k_{obs} due to increasing common-ion return.

In line with the preceding mechanistic analysis, Figure 5 shows that higher amine concentrations are needed to suppress common-ion return in the more concentrated substrate solutions. Remarkably, the first-order rate constants obtained at different substrate concentrations are almost identical ($k_{obs}([\mathbf{1e}]) = 18.6$ (1 mM), 17.7 (8 mM), and 17.2 s⁻¹ (18 mM)) in the presence of 0.19 M DMAP. As expected, the amine additives have a bigger effect on the observed rate

constants of the concentrated solutions of **1e** than on the more dilute solutions.

According to Figure 6, the “best-fit rate constant” k_{obs} for the solvolysis of 4-methoxy-4'-methylbenzhydryl chloride **1f** (18 mM) in 90A10W in the absence of amine is reduced by a factor of 2.5 when common-ion return was enhanced by the addition of 18 mM Bu₄N⁺Cl⁻. This rate reduction can be compensated by adding amine; in the presence of high chloride ion concentrations, more DMAP is needed to suppress ion recombinations.

The situation described in Figures 3d and 4, i.e., increase of k_{obs} with increasing concentrations of nucleophilic amines until a plateau or shallow maximum is reached, has been observed for numerous solvolysis reactions in aqueous acetone and aqueous acetonitrile (see the Supporting Information). Tables 2 and 3 list the maximum values of k_{obs} obtained with different amine additives. Because the maximum values of k_{obs} are reached at different amine concentrations, these rate constants do not refer to exactly the same reaction conditions because the nature of the solvent is slightly altered by the amines (up to 10 vol %). This is only a minute effect, however, compared with the large effects caused by the variation of the substituents in the substrates or variations of the water concentration in the solvents.

More severe are the uncertainties of some of the k_{obs} values in Tables 2 and 3, which have been obtained in the absence of amines. If they are printed in italics, they include a significant amount of common-ion return and thus are specific for the selected concentration of the substrate (here: 0.018 M). As described above, these k_{obs} values reflect a “best fit” to the

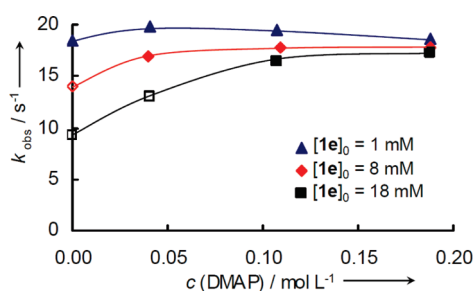
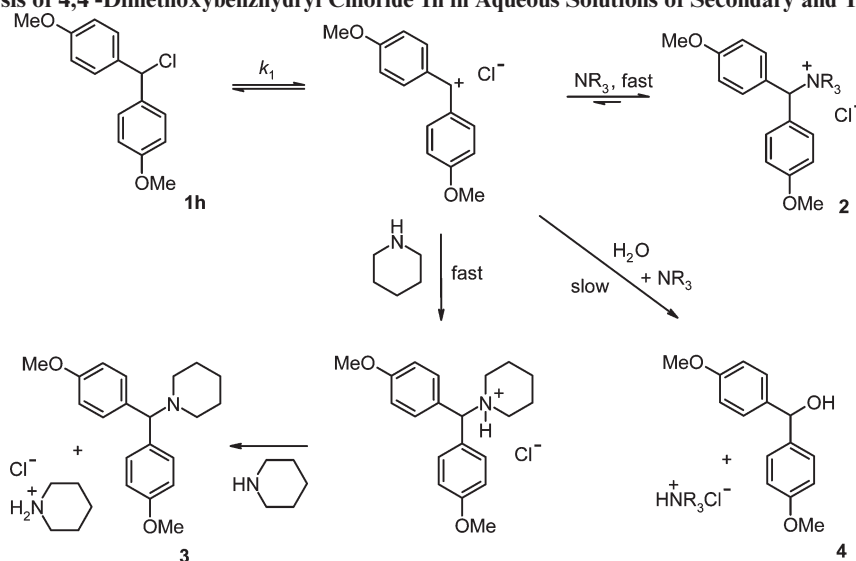
SCHEME 2. Heterolysis of 4,4'-Dimethoxybenzhydryl Chloride **1h** in Aqueous Solutions of Secondary and Tertiary Amines

FIGURE 5. Solvolysis of 4-methoxybenzhydryl chloride (**1e**) in 60A40W at 25 °C at different substrate concentrations in the presence of DMAP (open symbols represent kinetics that are not of first-order, see text).

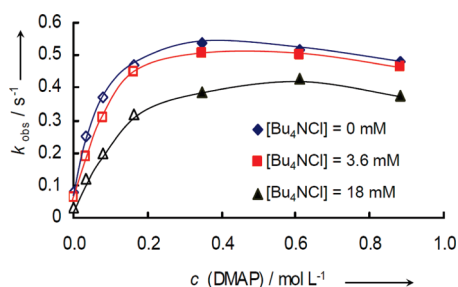


FIGURE 6. Solvolysis of 4-methoxy-4'-methylbenzhydryl chloride (**1f**, 0.018 M) in 90A10W at 25 °C in the presence of Bu_4NCl (open symbols represent kinetics that are not of first-order).

exponential function and thus give useful information about the gross reactivity at a certain substrate concentration, but are not real “constants”.

This trapping method also works with other strong nucleophiles like PPh_3 as can be seen in entry 10 of Table 2.

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Discussion

Qualitatively, the message from Tables 2 and 3 is clear: The effect of the amine additives increases as the solvolysis rate constants increase, i.e., as one moves from left to right in Tables 2 and 3. While the solvolyses of the methyl-substituted benzhydryl chlorides **1c** and **1d** (0.018 M) in 90% acetone (90A10W) are only accelerated by a factor of 1.2 to 1.4 by added DMAP (cf. entries 1 and 4 in Table 2), the amine effect increases gradually when moving from left to right and reaches a factor of 65 for benzhydryl chloride **1j**, which ionizes 6.5 orders of magnitude faster than **1c** (compare entries 1 and 4 in Table 2).

The increasing importance of common-ion return with decreasing reactivity of the carbocations has previously been considered as a consequence of the reactivity–selectivity principle, which claims that selectivity increases with decreasing reactivity. With the fall of the reactivity–selectivity principle¹⁷ a more sophisticated explanation becomes necessary.

In previous work,¹⁸ we have shown that eq 2 can be used to calculate the rate constants of the reactions of carbocations with a large variety of nucleophiles, including amines,¹⁹ halide ions,^{5b} and solvents.^{5a}

$$\log k = s(E+N) \quad (2)$$

where k is the second-order ($\text{M}^{-1} \text{s}^{-1}$) or first-order (s^{-1} , for reactions with solvents) rate constant (20 °C), s and N are the empirical, nucleophile-specific parameters, and E is the empirical electrophilicity parameter.

We will now employ eq 2 for rationalizing the effects reported in Tables 2 and 3.

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TABLE 2. Maximum First-Order Rate Constants ($k_{\text{obs,max}}$, s^{-1}) for the Solvolysis Reactions of the Benzhydryl Chlorides **1c–j** (0.018 M) in the Presence of Amines in Aqueous Acetone at 25 °C

	amine	1c	1d	1e	1f	1g	1h	1i	1j
90% acetone/10% water, v/v (90A10W)									
1	without amine ^a	1.1×10^{-4b}	1.4×10^{-3c}	1.6×10^{-2}	7.8×10^{-2}	1.7×10^{-1}	3.9×10^{-1}	2.2	6.2
2	piperidine				6.30×10^{-1}	2.64	2.50×10^1	1.01×10^2	
3	NEt ₃			4.43×10^{-2}	3.95×10^{-1}	1.68	1.36×10^1		2.89×10^2
4	DMAP	1.33×10^{-4}	1.89×10^{-3}	7.53×10^{-2d}	5.40×10^{-1}	2.09	1.45×10^1	1.04×10^2	4.00×10^2
5	DABCO			8.87×10^{-2}	5.81×10^{-1}	2.38	1.74×10^1		4.57×10^2
6	pyridine			7.89×10^{-2}	6.13×10^{-1}	2.29	1.59×10^1		
7	2,6-lutidine ^a						8.4×10^{-1}		
8	2-chloropyridine ^a			1.9×10^{-2}			5.4×10^{-1}	2.2	
9	Proton Sponge ^g						1.21×10^1		
10	PPh ₃						2.11×10^1		
80% acetone/20% water, v/v (80A20W)									
11	without amine ^a	1.1×10^{-3e}	2.3×10^{-2f}	3.3×10^{-1}	1.7	3.9	1.5×10^1		
12	piperidine			8.59×10^{-1}	5.56	1.58×10^1	1.57×10^2		
13	NEt ₃						9.58×10^1		
14	DMAP	1.62×10^{-3}	2.80×10^{-2}	9.46×10^{-1}	5.77	1.73×10^1	1.37×10^2		
15	DABCO			8.25×10^{-1}	5.67	1.76×10^1	1.60×10^2		
16	pyridine			9.16×10^{-1}	6.06	1.75×10^1	1.56×10^2		
17	2-chloropyridine ^a			3.2×10^{-1}					
60% acetone/40% water, v/v (60A40W)									
18	without amine ^a			9.2	3.8×10^1	6.3×10^1			
19	DMAP			1.71×10^1	8.40×10^1	1.74×10^2			
20	DABCO			1.47×10^1					

^aItalics: not first-order. ^bSolvolysis rate constants $k_1 = 1.11 \times 10^{-4}$ (from ref 9b), 1.12×10^{-4} (from ref 13), and $1.15 \times 10^{-4} \text{ s}^{-1}$ (from ref 14). ^cSolvolysis rate constants $k_1 = 1.83 \times 10^{-3}$ (from ref 9b) and $1.43 \times 10^{-3} \text{ s}^{-1}$ (from ref 13). ^dMeasured at the stopped-flow conductometer; at the conventional conductometer $k_{\text{obs,max}} = 7.23 \times 10^{-4} \text{ s}^{-1}$. ^eSolvolysis rate constants $k_1 = 1.76 \times 10^{-3}$ (from ref 9b), 1.64×10^{-3} (from ref 15), and $1.60 \times 10^{-3} \text{ s}^{-1}$ (from ref 16). ^fSolvolysis rate constant $k_1 = 2.79 \times 10^{-2} \text{ s}^{-1}$ (from ref 9b). ^g*N,N,N',N'*-Tetramethylnaphthalene-1,8-diamine.

TABLE 3. Maximum First-Order Rate Constants ($k_{\text{obs,max}}$, s^{-1}) for the Solvolyses of the Benzhydryl Chlorides **1a–h** ($6.1 \times 10^{-3} \text{ M}$) in the Presence of Amines in Aqueous Acetonitrile at 25 °C

	amine	1a	1b	1c	1d	1e	1g	1h
90% acetonitrile/10% water, v/v (90AN10W)								
1	without amine ^a		8.14×10^{-5}	2.50×10^{-3}	4.2×10^{-2}	4.7×10^{-1}	6.0	1.8×10^1
2	DABCO				4.42×10^{-2}	1.53	3.32×10^1	2.49×10^2
3	piperidine				4.36×10^{-2}	1.43	3.30×10^1	2.38×10^2
80% acetonitrile/20% water, v/v (80AN20W)								
4	without amine ^a	1.09×10^{-4}	8.03×10^{-4}	2.28×10^{-2}	3.41×10^{-1}	3.8	4.0×10^1	
5	DABCO				3.45×10^{-1}	7.70	1.20×10^2	
6	piperidine					7.76	1.12×10^2	
60% acetonitrile/40% water, v/v (60AN40W)								
7	without amine ^a	1.14×10^{-3}	8.29×10^{-3}	1.97×10^{-1}	2.6	2.8×10^1		
8	DABCO				2.76	4.08×10^1		
9	piperidine				2.63	3.56×10^1		

^aItalics: $k_{\text{obs,max}}$ was obtained from the “best fit” and does not reflect the real first-order rate constants (see text).

Figure 7 compares the pseudo-first-order rate constants (calculated by eq 2) for the reactions of benzhydrylium ions with solvents, chloride ions ($6.1 \times 10^{-3} \text{ M}$),²⁰ and DABCO (0.1 M). The correlation line for the solvent was calculated by eq 2 from the published reactivity parameters $N = 5.02$ and $s = 0.89$ for 80% acetonitrile/20% water^{5a} and the electrophilicity parameters E of the benzhydrylium ions **1a–j** (Table 1). Substitution of the published nucleophile-specific parameters $N = 13.30$ and $s = 0.60$ for the chloride ion in 80% acetonitrile^{5b} (80AN20W) and the electrophilicity

parameters E of the benzhydrylium ions **1a–j** (Table 1) into eq 2 yields the second-order rate constants, which are multiplied by the concentrations of Cl^- (6.1 mM)²⁰ to give the pseudo-first-order rate constants drawn in Figure 7. From the known nucleophilicity parameters N and s of secondary and tertiary amines in various solvents¹⁹ one can derive that in 0.1 M solutions of amines in aqueous acetonitrile, most amines react faster than water and chloride as illustrated for the reaction of DABCO with benzhydrylium ions in Figure 7. Only highly reactive carbocations, where the diffusion limit is close, will react faster with water that is present in higher concentration.

We can now use the graph shown in Figure 7 to rationalize the observed rate effects. In agreement with the previously

(20) This concentration corresponds to the final concentration of Cl^- at the end of the solvolysis reactions shown in Table 3, i.e. the maximum concentration of Cl^- during the measurement.

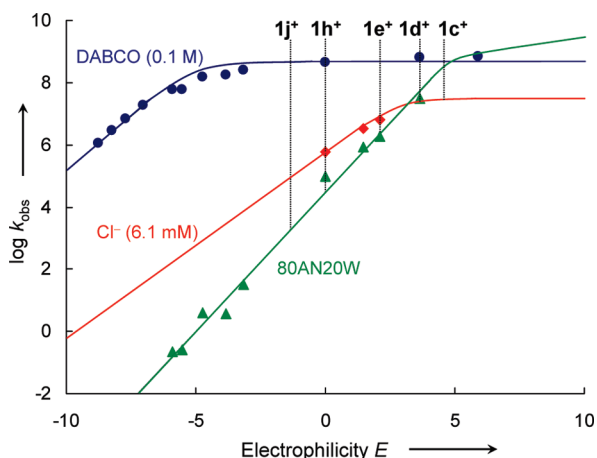


FIGURE 7. Rate constants ($\log k_{\text{obs}}$) for the reactions of benzhydrylium ions with 80% acetonitrile/20% water, chloride ion (6.1 mM),²⁰ and DABCO (0.1 M) plotted against the electrophilicity E of the benzhydrylium ions.

published small mass-law constants for the dimethyl-substituted benzhydryl chloride **1d** ($\alpha = k_{-1}/k_{\text{solv}} = 74 \text{ M}^{-1}$) and monomethyl-substituted benzhydryl chloride **1c** ($\alpha = 32 \text{ M}^{-1}$) in 80% acetone (80A20W),¹⁶ ion recombination does not play an important role in the hydrolyses of these two compounds in aqueous acetonitrile when dilute solutions (i.e., small $[\text{Cl}^-]$) are considered (for **1d**⁺ and **1c**⁺, the green solvent graph is above the red Cl^- graph in Figure 7). As a result, the solvolysis rates of these compounds are almost unaffected by the addition of amines (Tables 2 and 3). When methoxy-substituted benzhydrylium ions with $E \leq 2.1$ are considered, the solvent graph drops below the chloride graph in Figure 7, suggesting that common-ion return becomes important in aqueous acetonitrile, in agreement with the deviation of the solvolysis kinetics from the first-order rate law. Because Figure 7 shows that in this range the amine graph is far above the graphs for the solvent and for Cl^- , one can explain why moderate amine concentrations are already sufficient to suppress the common-ion return and thus lead to an increase of the solvolysis rates. As discussed earlier,^{5b} the different slopes of the chloride and solvent correlations account for the decreasing amount of ion return as one moves from left to right in Figure 7. The decreasing magnitude of the amine effect as one moves from left to right in Figure 7 can be explained analogously.

The preceding discussion suggests that the rate acceleration by added amines is due to suppression of the common-ion return. One might, therefore, expect the same plateau for all reactive amines in Figure 4. This is not the case, and Tables 2 and 3 show that the maximal first-order rate constants for the various benzhydryl systems in the presence of different amines differ up to a factor of 2. Most notable, the relative heights of the plateaus do not reflect the relative amine nucleophilicities. Thus, pyridine leads generally to slightly higher limiting rates than DMAP despite of its lower nucleophilicity^{19d} (see also Figure 4). These modest differences may be due to the fact that the amines intercept contact ion pairs as well as free ions. As the rates of most of these combinations of carbocations with amines are controlled by

diffusion and not by activation, it is not surprising that the heights of the plateaus do not correlate with the previously reported order of nucleophilicities of amines.¹⁹

Conclusion

Nucleophilic secondary and tertiary amines have been found to suppress common-ion return in the $\text{S}_{\text{N}}1$ reactions of rapidly ionizing benzhydryl chlorides without giving rise to $\text{S}_{\text{N}}2$ reactions. By employing amines as nonionic trapping agents for carbocations instead of the commonly used azide ions it has become possible to follow the kinetics by conductometry and thus measure fast ionization processes on the millisecond time scale, i.e., rates of formation of highly stabilized carbocations, for which only a few kinetic data have so far been available. In this way, it has become possible to close the gap between $\text{S}_{\text{N}}1$ reactions without common-ion return and carbocation-like transition states (Figure 1A) and $\text{S}_{\text{N}}2\text{C}^+$ reactions (Figure 1, C), where carbocations accumulate before they are trapped by the solvents or other nucleophiles.

Experimental Section

General. Solvolysis rates of the benzhydryl chlorides **1a–j** (Table 1) were monitored by following the increase of the conductivity of the reaction mixtures, using a conductometer with a Pt electrode. For the study of solvolysis reactions with half-lives of $10^{-2} \text{ s} < \tau_{1/2} < 10 \text{ s}$, a standard stopped-flow conductometer was used in single-mixing mode.

Dry acetone and acetonitrile for the kinetic experiments were purchased ($< 50 \text{ ppm}$ of H_2O) and used without further purification. Mixtures of solvents are given as (v/v) and the solvents are abbreviated: A = acetone, AN = acetonitrile, W = water. For example, the solvent mixture 80A20W refers to a mixture of acetone and water in a ratio of 80/20 (v/v).

Kinetic Experiments. For the study of slow reactions, solvent mixtures (20 mL) were thermostated ($\pm 0.1 \text{ }^\circ\text{C}$) at $25.0 \text{ }^\circ\text{C}$ for 5 min prior to adding the substrate. Typically, 10 to 80 mg of substrate was dissolved in $100 \mu\text{L}$ of acetone or acetonitrile, then injected into the solvent, and the conductance (G) was recorded at given time intervals. When the stopped-flow equipment was used, the benzhydryl chlorides were dissolved in pure acetone or acetonitrile and mixed in the conductivity cell with aqueous acetone or acetonitrile to give solutions of the desired composition.

To examine the consistency of the results determined with the two instruments, the kinetics of the solvolysis of 4-methoxybenzhydryl chloride **1e** in 90% acetone (90A10W) was studied at the conventional conductometer as well as at the stopped-flow instrument. Figure S3 (Supporting Information) shows that the results obtained with both instruments agreed within experimental error.

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