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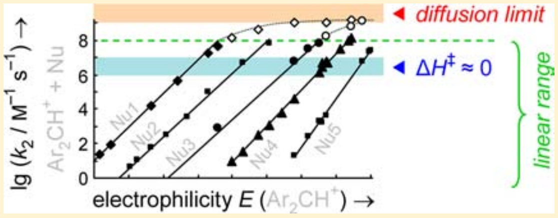
Free Energy Relationships for Reactions of Substituted Benzhydrylium Ions: From Enthalpy over Entropy to Diffusion Control

Johannes Ammer, Christoph Nolte, and Herbert Mayr*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), 81377 München, Germany

Supporting Information



ABSTRACT: Second-order rate constants k_2 for the reactions of various donor- and acceptor-substituted benzhydrylium ions Ar_2CH^+ with π-nucleophiles in CH_2Cl_2 were determined by laser flash irradiation of benzhydryl triarylphosphonium salts $Ar_2CH\text{-}PAr_3^+X^-$ in the presence of a large excess of the nucleophiles. This method allowed us to investigate fast reactions up to the diffusional limit including reactions of highly reactive benzhydrylium ions with *m*-fluoro and *p*-(trifluoromethyl) substituents. The rate constants determined in this work and relevant literature data were jointly subjected to a correlation analysis to derive the electrophilicity parameters E for acceptor-substituted benzhydrylium ions, as defined by the linear free energy relationship $\log k_2(20\ °\mathrm{C}) = s_N(N + E)$. The new correlation analysis also leads to the N and s_N parameters of 18 π-nucleophiles, which have only vaguely been characterized previously. The correlations of $\log k_2$ versus E are linear well beyond the range where the activation enthalpies $\Delta H^{\ddagger}$ of the reactions are extrapolated to reach the value of $\Delta H^{\ddagger} = 0$, showing that the change from enthalpy control to entropy control does not cause a bend in the linear free energy relationship, a novel manifestation of the compensation effect. A flattening of the correlation lines only occurs for $k_2 > 10^8$ M^{-1} s^{-1} when the diffusion limit is approached.

INTRODUCTION

Reactions of benzhydrylium ions (Ar_2CH^+) with a large variety of π-nucleophiles in CH_2Cl_2 have been used to construct the most wide-stretching linear free energy relationships presently known.[1] Using eq 1, it has become possible to predict second-order rate constants k_2 (M^{-1} s^{-1}) of reactions of electrophiles with nucleophiles by means of one electrophile-specific parameter E and two solvent-dependent nucleophile-specific parameters N and s_N.[1]

$$\log k_2(20\ °\mathrm{C}) = s_N(N + E) \tag{1}$$

Since the beginning of this work,[1a,b] the scope of electrophiles characterized by eq 1 has been extended considerably. Apart from the benzhydrylium ions $\mathbf{E}(\mathbf{1}\text{–}\mathbf{26})^+$ which were employed as reference electrophiles in the original work (Table 1),[1b,2] eq 1 has been applied to many other classes of electrophiles,[1c–f] including allyl cations,[1c,3] reactions of tritylium ions with sterically nondemanding nucleophiles,[4] iminium ions,[1c,5] carboxonium ions,[1c] dithiocarbenium ions,[1c] and cationic metal-π-complexes.[1c,6] Equation 1 is also applicable to reactions of neutral carbon electrophiles such as acceptor-substituted arenes,[7] aldehydes,[8] imines,[8] and acceptor-substituted ethylenes such as quinone methides,[9a,b] benzylidenemalononitriles,[1f] 2-benzylideneindan-1,3-diones,[1f] benzylidenebarbituric and -thiobarbituric acids,[1f] benzylidene Meldrum's acids,[9c] benzylidenemalonates,[9d] 1,2-diaza-1,3-dienes,[9e] *trans*-β-nitrostyrenes,[9f] and bissulfonyl ethylenes.[9g] Equation 1 has furthermore been employed to describe reactions of carbon nucleophiles with heteroatom electrophiles like diazonium ions,[1c] azodicarboxylates,[10] and chlorinating agents.[11] Currently, the electrophilicity scale defined by eq 1 encompasses a range of 30 orders of magnitude ($-24 \le E \le +6$).[12]

The most reactive electrophiles characterized so far were alkyl-substituted benzyl cations ($E \approx 5.7$–9.6)[13] and tertiary alkyl cations ($E \approx 7.5$–9.0),[14] but all electrophilicity parameters of highly reactive carbenium ions with $E > 6$ were only indirectly obtained by competition experiments. Direct measurements of rate constants for reactions of acceptor-substituted benzhydrylium ions ($E > 6$) with nucleophiles turned out to be a veritable challenge due to the low stabilities and high reactivities of these carbocations.[14–17] We have recently reported an efficient method to generate the highly reactive benzhydrylium ions $\mathbf{E}(\mathbf{27}\text{–}\mathbf{33})^+$ by laser flash photolysis of the triarylphosphonium salts $\mathbf{E}\text{-}PAr_3^+X^-$ in CH_2Cl_2 (Scheme 1).[18] This method will be used in this work to determine the second-order rate constants k_2 for the reactions of highly reactive benzhydrylium ions $\mathbf{E}^+$ with a variety of nucleophiles $\mathbf{N}$ in order to provide quantitative information about their electrophilic reactivities. In this way, it has become possible to investigate free energy relationships in reaction series stretching from slow reactions proceeding within hours to the fastest bimolecular reactions, which are controlled by diffusion. The conclusions derived therefrom will be crucial

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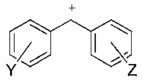
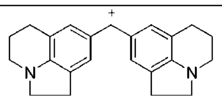
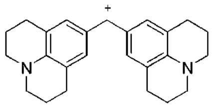
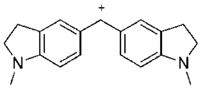
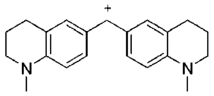
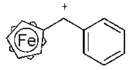
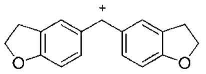
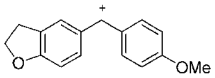
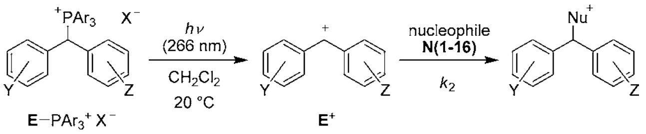
Table 1. Electrophiles $E(1-33)^+$ and Their Electrophilicity Parameters E

no.	abbreviation[a]	 Y	Z	E
$E1^+$	$(lil)_2CH^+$			-10.04^b
$E2^+$	$(jul)_2CH^+$			-9.45^b
$E3^+$	$(ind)_2CH^+$			-8.76^b
$E4^+$	$(thq)_2CH^+$			-8.22^b
$E5^+$	$(pyr)_2CH^+$	Y = Z = 4-(N-pyrrolidino)		-7.69^b
$E6^+$	$(dma)_2CH^+$	Y = Z = 4-N(Me)$_2$		-7.02^b
$E7^+$	$(mpa)_2CH^+$	Y = Z = 4-N(Me)(Ph)		-5.89^b
$E8^+$	$(mor)_2CH^+$	Y = Z = 4-(N-morpholino)		-5.53^b
$E9^+$	$(dpa)_2CH^+$	Y = Z = 4-N(Ph)$_2$		-4.72^b
$E10^+$	$(mfa)_2CH^+$	Y = Z = 4-N(Me)(CH$_2$CF$_3$)		-3.85^b
$E11^+$	$(pfa)_2CH^+$	Y = Z = 4-N(Ph)(CH$_2$CF$_3$)		-3.14^b
$E12^+$	$fc(Ph)CH^+$			-2.64^b
$E13^+$	$(fur)_2CH^+$			-1.36^b
$E14^+$	$fur(ani)CH^+$			-0.81^c
$E15^+$	$(ani)_2CH^+$	4-MeO	4-MeO	0.00^b
$E16^+$	$ani(pop)CH^+$	4-MeO	4-PhO	0.61^b
$E17^+$	$ani(tol)CH^+$	4-MeO	4-Me	1.48^b
$E18^+$	$ani(Ph)CH^+$	4-MeO	H	2.11^b
$E19^+$	$pop(Ph)CH^+$	4-PhO	H	2.90^b
$E20^+$	$(tol)_2CH^+$	4-Me	4-Me	3.63^b
$E21^+$	$tol(Ph)CH^+$	4-Me	H	4.43^c
$E22^+$	$(pfp)_2CH^+$	4-F	4-F	5.01^c
$E23^+$	$pfp(Ph)CH^+$	4-F	H	5.20^c
$E24^+$	–	3-F, 4-Me	3-F, 4-Me	5.24^c
$E25^+$	Ph_2CH^+	H	H	5.47^c
$E26^+$	$(pcp)_2CH^+$	4-Cl	4-Cl	5.48^c
$E27^+$	$mfp(Ph)CH^+$	3-F	H	6.23^c
$E28^+$	$tfm(Ph)CH^+$	4-(CF$_3$)	H	6.70^c
$E29^+$	$dfp(Ph)CH^+$	3,5-F$_2$	H	6.74^c
$E30^+$	$(mfp)_2CH^+$	3-F	3-F	6.87^c
$E31^+$	$dfp(mfp)CH^+$	3,5-F$_2$	3-F	7.52^c
$E32^+$	$(tfm)_2CH^+$	4-(CF$_3$)	4-(CF$_3$)	$(7.96)^{c,d}$
$E33^+$	$(dfp)_2CH^+$	3,5-F$_2$	3,5-F$_2$	$(8.02)^{c,d}$

[a]Abbreviations as introduced in ref 1b and three new abbreviatons: mfp = 3-fluorophenyl, dfp = 3,5-difluorophenyl, tfm = 4-(trifluoromethyl)phenyl. [b]From ref 1b. [c]New or revised E parameters from this work. [d]Approximate values.

Scheme 1. Generation of Benzhydrylium Ions E^+ by Laser Flash Irradiation of the Phosphonium Salts $E\text{-}PAr_3^+X^-$ [a]



[a]Ar = Ph or 4-Cl-C_6H_4; X^- = BF_4^- or SbF_6^-.

for the development of theoretical models of polar organic reactivity.

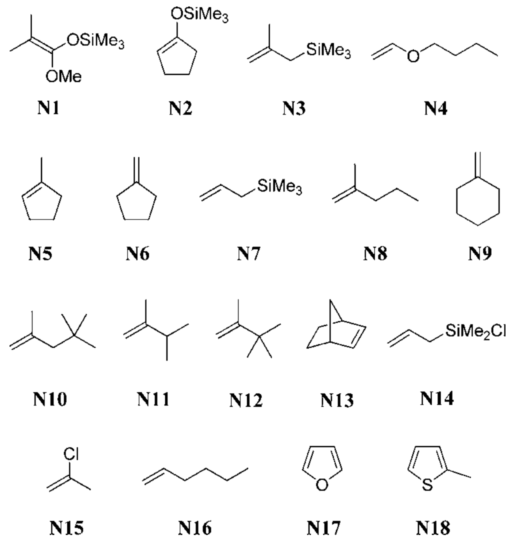
RESULTS AND DISCUSSION

Kinetics of the Reactions of Benzhydrylium Ions with π-Nucleophiles in CH_2Cl_2. The presently available electrophilicity and nucleophilicity parameters (eq 1) were derived from the second-order rate constants of the reactions of the benzhydrylium ions $E(1-13)^+$, $E(15-21)^+$, $E23^+$, $E25^+$, and $E26^+$ ($-10 \leq E \leq +6$, Table 1) with a variety of π-nucleophiles in dichloromethane solution.[1b] For the inclusion of acceptor-substituted benzhydryl cations into the electrophilicity scale, we now determined the second-order rate constants for the reactions of these carbocations with the same class of π-nucleophiles in CH_2Cl_2 at 20 °C.

Electrophiles. Indirectly determined estimates of electrophilicity parameters for two m-chloro-substituted benzhydrylium ions were previously published,[14] but further use of these compounds has been discouraged because they may cause severe skin irritations.[19a] For that reason, we now recommend the m-fluoro-substituted benzhydrylium ions $E(27,30,31,33)^+$ as reference systems.[20] Other m-fluoro- ($E24^+$ and $E29^+$) and p-(trifluoromethyl)-substituted systems ($E28^+$ and $E32^+$) were investigated for comparison. We further included $E14^+$ and $E22^+$ as new reference electrophiles, and determined additional rate constants for the reactions of $E(21-23)^+$ and $E(25,26)^+$ because only limited data were available for each of these benzhydryl cations at the time of the original correlation analysis.[1b]

Nucleophiles. Chart 1 shows the π-nucleophiles **N(1−18)** which were used for the kinetic investigations in this study. Some of them were already employed as reference nucleophiles in our prior work.[1b] The characterization of electrophiles with $E > 4$ requires nucleophiles in the range of $N < 4$, but there are additional restrictions. Nucleophiles which absorb at the excitation wavelength of the laser (e.g., **N17**, **N18**, or compounds containing phenyl groups) were not used for the laser flash photolysis experiments because they interfere with the photogeneration of the carbocations. Many of the remaining well-characterized nucleophiles in the range of $N < 4$ were not recommended as reference nucleophiles in ref 1b owing to their volatility or their tendency to undergo side reactions. Therefore, we have also studied reactions of E^+ with several other π-nucleophiles which have been characterized only poorly in our previous work. All π-nucleophiles used in this study could be obtained commercially, except **N12** which was prepared by a literature procedure.[21]

Chart 1. π-Nucleophiles Used in This Study



Kinetic Measurements. The benzhydrylium ions $\mathbf{E(13{-}30)^+}$ $(-2 < E < 7)$ were generated in CH_2Cl_2 solution by irradiation of the triphenylphosphonium tetrafluoroborates $\mathbf{E(13{-}30)}$-$PPh_3^+BF_4^-$ (Scheme 1) with a 7-ns pulse from the fourth harmonic of a Nd/YAG laser (λ_{exc} = 266 nm, 30−60 mJ/pulse).[18] As previously reported, the highly electrophilic benzhydrylium ions $\mathbf{E(31{-}33)^+}$ with $E > 7$ could only be generated efficiently when $P(p\text{-}Cl\text{-}C_6H_4)_3$ instead of PPh_3 was employed as the photoleaving group.[18] Since the highly reactive benzhydrylium ions $\mathbf{E32^+}$ and $\mathbf{E33^+}$ are consumed by reaction with BF_4^- so rapidly that they cannot be observed UV/vis-spectroscopically on the nanosecond time scale, the investigation of these carbocations additionally required the use of SbF_6^- as counteranion instead of BF_4^-.[18]

When the benzhydrylium ions $\mathbf{E(13{-}33)^+}$ were generated by irradiation of $\mathbf{E(13{-}33)}$-$PAr_3^+X^-$ (Ar = Ph or p-Cl-C_6H_4, $X^- = BF_4^-$ or SbF_6^-) in the presence of a large excess of the nucleophiles $\mathbf{N(1{-}16)}$, we typically observed monoexponential decays of the absorbances of the benzhydrylium ions, as illustrated in Figure 1a for the most electrophilic benzhydrylium ion of this series, $\mathbf{E33^+}$, in the presence of 5.26×10^{-2} M allylchlorodimethylsilane (**N14**). The pseudo-first-order rate constants k_{obs} (s^{-1}) were obtained by fitting exponential decay functions to the experimental data. Plots of k_{obs} versus the concentrations of the nucleophiles were linear (Figure 1b) in all cases, and the slopes of these plots provided the second-order rate constants k_2 ($M^{-1}\ s^{-1}$) which are listed in Table 2 (below). Although the benzhydrylium ions $\mathbf{E^+}$ generated by photolysis of $\mathbf{E}$-$PAr_3^+X^-$ may exist as ion pairs $\mathbf{E^+}X^-$ in CH_2Cl_2 solution, it was shown that the rate constants k_2 for the reactions of $\mathbf{E^+}$ with added π-nucleophiles are independent of the nature of X^- and the degree of ion-pairing.[18] Benzhydryl radicals which are formed as byproducts of the photolysis of the phosphonium salts do not affect the kinetics. The UV/vis absorption bands of the benzhydryl radicals ($\lambda_{max} \approx$ 327−344 nm) never overlap with those of the benzhydryl cations ($\lambda_{max} >$ 420 nm).[18] Moreover, the reactions of radicals with π-systems are known to be much slower than the reactions of the structurally analogous carbocations[19b] and, therefore, do not affect the effective concentrations of the π-nucleophiles.

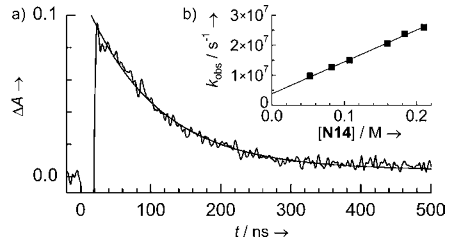
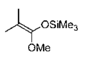
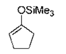
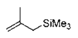
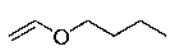
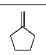
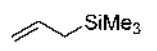
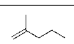
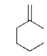
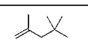
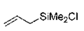
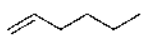


Figure 1. (a) Decay of the absorbance of $\mathbf{E33^+}$ at λ = 445 nm observed after irradiation of a 6.85×10^{-5} M solution of $\mathbf{E33}$−$P(p\text{-}Cl\text{-}C_6H_4)_3^+SbF_6^-$ in CH_2Cl_2 in the presence of 5.26×10^{-2} M **N14** and exponential fit of the data ($k_{obs} = 9.68 \times 10^6\ s^{-1}$, $R^2 = 0.9873$). (b) Plot of the pseudo-first-order rate constants k_{obs} for the reactions of $\mathbf{E33^+}$ with **N14** in CH_2Cl_2 against the concentrations of **N14** ($k_{obs} = 1.06 \times 10^8[\mathbf{N14}] + 3.88 \times 10^6$, $R^2 = 0.9979$).

Background Reactions. The positive intercepts of the k_{obs} versus [**N**] plots correspond to the rate constants k_0 (s^{-1}) for the background reactions without added nucleophile, which may be reactions with the BF_4^- anions of the phosphonium salts or with impurities that are still present in the rigorously purified CH_2Cl_2.[18] With increasing electrophilicity of the carbocations $\mathbf{E^+}$, these background reactions become faster, which sets a lower limit for the determination of the second-order rate constants k_2 by this method, because the bimolecular reactions of interest must be able to compete with the background reactions. For the most electrophilic benzhydrylium ions in our series, $\mathbf{E32^+}$ and $\mathbf{E33^+}$, k_0 is in the range of $(4{-}8) \times 10^6\ s^{-1}$ when the carbocations are generated from $\mathbf{E(32,33)}$-$P(p\text{-}Cl\text{-}C_6H_4)_3^+SbF_6^-$ in CH_2Cl_2. As a consequence of these fast background reactions, there is only a very limited group of nucleophiles **N** which react fast enough to determine k_2 but slow enough to stay below the diffusion-controlled regime (see below). Moreover, reactions of $\mathbf{E^+}$ with suitable nucleophiles **N** can only compete with the background reaction when the nucleophiles are employed in sufficiently high concentrations, since k_2[**N**] must be of comparable magnitude as k_0.

Another restriction for the determination of rate constants with the laser flash photolysis technique is imposed by the recombination of the photogenerated carbocations $\mathbf{E^+}$ with the photoleaving group PAr_3 which occurs on time scales ≥∼10 μs at typical concentrations of the photofragments in our experiments.[18] As $\mathbf{E^+}$ and PAr_3 are generated in equimolar amounts (10^{-6}−10^{-5} M) by the laser pulse, the reaction of $\mathbf{E^+}$ with PAr_3 is not of first order, and a nonexponential decay of $\mathbf{E^+}$ is observed in these cases. Thus, even with moderately stabilized carbocations, such as $\mathbf{E(13{-}21)^+}$, there is a lower limit of $(1{-}5) \times 10^5\ s^{-1}$ for the pseudo-first-order rate constants k_{obs} that can be determined by a monoexponential fit of the experimental data, because slower reactions of $\mathbf{E^+}$ show more complicated decay kinetics due to the concurrent diffusion-controlled second-order reaction of $\mathbf{E^+}$ with PAr_3.[18] The second-order rate constant $k_2 = 5.6 \times 10^5\ M^{-1}\ s^{-1}$ for the reaction of $\mathbf{E20^+}$ with **N5**, for example, was obtained by fitting the decay of [$\mathbf{E20^+}$] to a kinetic model consisting of two second-order processes for the reactions of $\mathbf{E20^+}$ with **N5** ($\mathbf{E20^+}$ + **N5**, second-order rate constant k_2) and with PPh_3 ($\mathbf{E20^+} + PPh_3 \rightarrow \mathbf{E20}\text{-}PPh_3^+$, second-order rate constant $k_{phosphine}$) using the software package Gepasi[24] (see Supporting Information for details). Second-order reactions of benzhydrylium ions ($E \geq 0$) which proceed slower than $\sim 5 \times 10^5\ M^{-1}\ s^{-1}$ cannot be evaluated reliably, because even in the presence of

Table 2. Second-Order Rate Constants k_2 (M^{-1} s^{-1}) for Reactions of Electrophiles E^+ with π-Nucleophiles and Comparison with Rate Constants k_{calc} (M^{-1} s^{-1}) Calculated from Equation 1[a]

	nucleophile			electrophile		experiment	correlation analysis	
N	formula	N, s_N	E^+	abbreviation	E	k_2[b] / M^{-1} s^{-1}	k_{calc}[c] / M^{-1} s^{-1}	k_{calc}/k_2
N1		$N = 9.00$[d]	**E13**$^+$	(fur)$_2$CH$^+$	−1.36[d]	1.86×10^{7}	3.07×10^{7}	1.65
		$s_N = 0.98$[d]	**E14**$^+$	fur(ani)CH$^+$	−0.81	4.47×10^{7}	1.06×10^{8}	2.38
			E15$^+$	(ani)$_2$CH$^+$	0.00[d]	1.54×10^{8}	(6.61×10^{8})	(4.29)
			E17$^+$	ani(tol)CH$^+$	1.48[d]	4.15×10^{8}	(1.86×10^{10})	(44.9)
			E20$^+$	(tol)$_2$CH$^+$	3.63[d]	1.02×10^{9}	(2.38×10^{12})	(2.3×10^{3})
			E25$^+$	(Ph)$_2$CH$^+$	5.47	1.15×10^{9}	(1.52×10^{14})	(1.3×10^{5})
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.52×10^{9}	(3.57×10^{15})	(2.3×10^{6})
N2		$N = 6.57$[d]	**E16**$^+$	ani(pop)CH$^+$	0.61[d]	5.34×10^{6}	4.76×10^{6}	0.89
		$s_N = 0.93$[d]	**E18**$^+$	ani(Ph)CH$^+$	2.11[d]	6.64×10^{7}	1.18×10^{8}	1.78
			E20$^+$	(tol)$_2$CH$^+$	3.63[d]	3.00×10^{8}	(3.06×10^{9})	(10.2)
			E25$^+$	(Ph)$_2$CH$^+$	5.47	9.39×10^{8}	(1.57×10^{11})	(168)
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.73×10^{9}	(3.16×10^{12})	(1.8×10^{3})
N3		$N = 4.41$[d]	**E20**$^+$	(tol)$_2$CH$^+$	3.63[d]	2.81×10^{7}	5.23×10^{7}	1.86
		$s_N = 0.96$[d]	**E21**$^+$	tol(Ph)CH$^+$	4.43	1.23×10^{8}	(3.06×10^{8})	(2.49)
			E25$^+$	(Ph)$_2$CH$^+$	5.47	3.97×10^{8}	(3.05×10^{9})	(7.69)
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.14×10^{9}	(6.74×10^{10})	(59.1)
			E31$^+$	dfp(mfp)CH$^+$	7.52	1.21×10^{9}	(2.48×10^{11})	(243)
N4		$N = 3.76$	**E9**$^+$	(dpa)$_2$CH$^+$	4.72[d]	1.06×10^{-1}[e]	1.34×10^{-1}	1.26
		$s_N = 0.91$	**E10**$^+$	(mfa)$_2$CH$^+$	−3.85[d]	7.49×10^{-1}[f]	8.28×10^{-1}	1.11
			E14$^+$	fur(ani)CH$^+$	0.81	7.65×10^{2}[g]	4.84×10^{2}	0.63
			E20$^+$	(tol)$_2$CH$^+$	3.63[d]	6.51×10^{6}	5.31×10^{6}	0.82
			E21$^+$	tol(Ph)CH$^+$	4.43	3.09×10^{7}	2.84×10^{7}	0.92
			E22$^+$	(pfp)$_2$CH$^+$	5.01	6.37×10^{7}	9.57×10^{7}	1.50
			E25$^+$	(Ph)$_2$CH$^+$	5.47	1.59×10^{8}	(2.51×10^{8})	(1.58)
			E26$^+$	(pcp)$_2$CH$^+$	5.48	1.60×10^{8}	(2.56×10^{8})	(1.60)
			E30$^+$	(mfp)$_2$CH$^+$	6.87	6.58×10^{8}	(4.71×10^{9})	(8.82)
			E31$^+$	dfp(mfp)CH$^+$	7.52	1.35×10^{9}	(1.84×10^{10})	(13.6)
N5		$N = 1.18$	**E20**$^+$	(tol)$_2$CH$^+$	3.63[d]	5.6×10^{5}[h]	4.24×10^{5}	0.76
		$s_N = 1.17$	**E21**$^+$	tol(Ph)CH$^+$	4.43	6.13×10^{6}	3.66×10^{6}	0.60
			E22$^+$	(pfp)$_2$CH$^+$	5.01	1.53×10^{7}	1.75×10^{7}	1.14
			E23$^+$	pfp(Ph)CH$^+$	5.20	3.49×10^{7}	2.91×10^{7}	0.84
			E24$^+$	–	5.24	3.17×10^{7}	3.25×10^{7}	1.02
			E25$^+$	(Ph)$_2$CH$^+$	5.47	5.91×10^{7}	6.03×10^{7}	1.02
			E26$^+$	(pcp)$_2$CH$^+$	5.48	4.72×10^{7}	6.20×10^{7}	1.31
			E27$^+$	mfp(Ph)CH$^+$	6.23	1.76×10^{8}	(4.67×10^{8})	(2.66)
			E30$^+$	(mfp)$_2$CH$^+$	6.87	5.87×10^{8}	(2.62×10^{9})	(4.47)
			E31$^+$	dfp(mfp)CH$^+$	7.52	1.33×10^{9}	(1.51×10^{10})	(11.4)
N6		$N = 2.82$	**E27**$^+$	mfp(Ph)CH$^+$	6.23	1.44×10^{8}	(1.13×10^{8})	(0.79)
		$s_N = 0.89$						
N7		$N = 1.68$	**E14**$^+$	fur(ani)CH$^+$	0.81	9.95[i]	7.41	0.75
		$s_N = 1.00$	**E21**$^+$	tol(Ph)CH$^+$	4.43	2.49×10^{6}	1.29×10^{6}	0.52
			E22$^+$	(pfp)$_2$CH$^+$	5.01	5.68×10^{6}	4.90×10^{6}	0.86
			E23$^+$	pfp(Ph)CH$^+$	5.20	1.06×10^{7}	7.59×10^{6}	0.72
			E24$^+$		5.24	9.17×10^{6}	8.32×10^{6}	0.91
			E25$^+$	(Ph)$_2$CH$^+$	5.47	1.50×10^{7}[j]	1.41×10^{7}	0.94
			E26$^+$	(pcp)$_2$CH$^+$	5.48	1.54×10^{7}	1.45×10^{7}	0.94
			E27$^+$	mfp(Ph)CH$^+$	6.23	6.19×10^{7}	8.13×10^{7}	1.31
			E28$^+$	tfm(Ph)CH$^+$	6.70	1.52×10^{8}	(2.40×10^{8})	(1.58)
			E30$^+$	(mfp)$_2$CH$^+$	6.87	2.13×10^{8}	(3.55×10^{8})	(1.67)
N8		$N = 0.84$	**E22**$^+$	(pfp)$_2$CH$^+$	5.01	1.33×10^{6}	1.59×10^{6}	1.19
		$s_N = 1.06$	**E23**$^+$	pfp(Ph)CH$^+$	5.20	4.55×10^{6}	2.53×10^{6}	0.56
			E24$^+$	–	5.24	2.79×10^{6}	2.78×10^{6}	1.00
			E25$^+$	(Ph)$_2$CH$^+$	5.47	5.69×10^{6}	4.88×10^{6}	0.86
			E26$^+$	(pcp)$_2$CH$^+$	5.48	5.00×10^{6}	5.00×10^{6}	1.00
			E27$^+$	mfp(Ph)CH$^+$	6.23	2.95×10^{7}	3.12×10^{7}	1.06
			E28$^+$	tfm(Ph)CH$^+$	6.70	9.51×10^{7}	9.83×10^{7}	1.03
			E29$^+$	dfp(Ph)CH$^+$	6.74	9.16×10^{7}	1.08×10^{8}	1.18
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.37×10^{8}	(1.49×10^{8})	(1.09)
N9		$N = 1.16$	**E22**$^+$	(pfp)$_2$CH$^+$	5.01	2.26×10^{6}	2.61×10^{6}	1.16
		$s_N = 1.04$	**E25**	(Ph)$_2$CH$^+$	5.47	9.86×10^{6}	7.86×10^{6}	0.80
			E27$^+$	mfp(Ph)CH$^+$	6.23	4.68×10^{7}	4.85×10^{7}	1.04
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.47×10^{8}	(2.24×10^{8})	(1.53)
			E31$^+$	dfp(mfp)CH$^+$	7.52	3.47×10^{8}	(1.06×10^{9})	(3.07)
N10		$N = 0.79$	**E22**$^+$	(pfp)$_2$CH$^+$	5.01	1.50×10^{6}	1.61×10^{6}	1.07
		$s_N = 1.07$	**E25**$^+$	(Ph)$_2$CH$^+$	5.47	6.61×10^{6}	4.99×10^{6}	0.76
			E27$^+$	mfp(Ph)CH$^+$	6.23	2.91×10^{7}	3.25×10^{7}	1.12
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.82×10^{8}	(1.57×10^{8})	(0.86)
N11		$N = 0.65$	**E25**$^+$	(Ph)$_2$CH$^+$	5.47	1.93×10^{6}	1.32×10^{6}	0.68
		$s_N = 1.00$	**E26**$^+$	(pcp)$_2$CH$^+$	5.48	1.46×10^{6}	1.35×10^{6}	0.92
			E27$^+$	mfp(Ph)CH$^+$	6.23	1.11×10^{7}	7.59×10^{6}	0.68
			E28$^+$	tfm(Ph)CH$^+$	6.70	2.11×10^{7}	2.24×10^{7}	1.06
			E29$^+$	dfp(Ph)CH$^+$	6.74	2.35×10^{7}	2.45×10^{7}	1.04
			E30$^+$	(mfp)$_2$CH$^+$	6.87	4.11×10^{7}	3.31×10^{7}	0.81
			E31$^+$	dfp(mfp)CH$^+$	7.52	8.24×10^{7}[j]	1.48×10^{8}	1.80
N12		$N = 0.06$	**E25**$^+$	(Ph)$_2$CH$^+$	5.47	2.16×10^{6}	8.26×10^{5}	0.38
		$s_N = 1.07$	**E27**$^+$	mfp(Ph)CH$^+$	6.23	6.32×10^{6}	5.37×10^{6}	0.85
			E30$^+$	(mfp)$_2$CH$^+$	6.87	2.42×10^{7}	2.60×10^{7}	1.07
			E31$^+$	dfp(mfp)CH$^+$	7.52	7.52×10^{7}	1.29×10^{8}	1.72
N13		$N = 0.25$	**E25**$^+$	(Ph)$_2$CH$^+$	5.47	6.96×10^{5}	4.90×10^{5}	0.70
		$s_N = 1.09$	**E27**$^+$	mfp(Ph)CH$^+$	6.23	3.57×10^{6}	3.30×10^{6}	0.92
			E28$^+$	tfm(Ph)CH$^+$	6.70	1.20×10^{7}	1.07×10^{7}	0.89
			E29$^+$	dfp(Ph)CH$^+$	6.74	1.42×10^{7}	1.19×10^{7}	0.84
			E30$^+$	(mfp)$_2$CH$^+$	6.87	1.51×10^{7}	1.64×10^{7}	1.09
			E31$^+$	dfp(mfp)CH$^+$	7.52	5.24×10^{7}	8.40×10^{7}	1.60
			E32$^+$	(tfm)$_2$CH$^+$	(7.96)[k]	1.15×10^{8}	(2.53×10^{8})	(2.20)
			E33$^+$	(dfp)$_2$CH$^+$	(8.02)[k]	1.24×10^{8}	(2.95×10^{8})	(2.38)
N14		$N = -0.57$	**E31**$^+$	dfp(mfp)CH$^+$	7.52	3.94×10^{7}	2.33×10^{7}	0.59
		$s_N = 1.06$	**E32**$^+$	(tfm)$_2$CH$^+$	(7.96)[k]	6.17×10^{7}	6.81×10^{7}	1.10
			E33$^+$	(dfp)$_2$CH$^+$	(8.02)[k]	1.06×10^{8}	(7.89×10^{7})	(0.74)
N15		$N = -3.65$	**E31**$^+$	dfp(mfp)CH$^+$	7.52	6.68×10^{7}	4.21×10^{7}	0.63
		$s_N = 1.97$	**E32**$^+$	(tfm)$_2$CH$^+$	(7.96)[k]	1.20×10^{8}	(3.10×10^{8})	(8.08)
N16		$N = -2.77$	**E22**$^+$	(pfp)$_2$CH$^+$	5.01	1.95×10^{3}[l]	1.44×10^{3}	0.74
		$s_N = 1.41$	**E31**$^+$	dfp(mfp)CH$^+$	7.52	5.77×10^{6}	4.98×10^{6}	0.86
			E32$^+$	(tfm)$_2$CH$^+$	(7.96)[k]	2.31×10^{7}	2.08×10^{7}	0.90
			E33$^+$	(dfp)$_2$CH$^+$	(8.02)[k]	2.54×10^{7}	[m]	[m]
N17		$N = 1.33$	**E14**$^+$	fur(ani)CH$^+$	−0.81	3.41[f]	4.69	1.37
		$s_N = 1.29$						
N18		$N = 1.35$	**E14**$^+$	fur(ani)CH$^+$	−0.81	6.18[f]	3.42	0.55
		$s_N = 0.99$						

[a] A complete list of rate constants used in the correlation analysis is given in Table S3.1 in the Supporting Information. [b] Unless noted otherwise: Laser flash photolysis of benzhydryl triarylphosphonium salts, this work; only rate constants with log $k_2 \leq 8.0$ were used for the correlation analysis. [c] Calculated from eq 1. Calculated values for rate constants $k_2 > 1.0 \times 10^8$ M^{-1} s^{-1} are shown in parentheses as eq 1 does not account for the limiting effect of diffusion. [d] These values were kept fixed to values obtained from the original correlation analysis.[1b] [e] From ref 22. [f] Conventional UV/vis spectrophotometry, this work. [g] Stopped-flow UV/vis measurement, this work. [h] Determined from nonexponential decay curves as the reaction of **E20**$^+$ with **N5** does not follow pseudo-first-order kinetics due to recombination of **E20**$^+$ with the photoleaving group PPh_3. See section S2.5 in the Supporting Information for details. [i] From ref 23a. [j] From ref 18. [k] These E parameters are based on only one or two rate constants, as reactions with $k_2 > 10^8$ M^{-1} s^{-1} were not included in the correlations. [l] From ref 15. [m] $k_{calc} = k_2$ since this is the only rate constant used for determining the E parameter of **E33**$^+$.

high nucleophile concentrations the reaction with the photoleaving group PAr_3 is observed almost exclusively.

Diffusion Limit. Besides the experimental limits discussed above and the upper limit accessible by our instrumentation ($k_{obs} \approx 3 \times 10^7$ s^{-1}), there is another more fundamental limitation that needs to be considered for a quantitative description of reactivities: In very fast reactions, the reaction rates are controlled by the rate of the diffusive approach of the reactants and not by the intrinsic reactivities of the reaction partners. Although **N1** reacts almost 40,000 times faster with stabilized benzhydrylium ions than **N3**,[1b] we measured almost the same rate constants $k_2 \approx (1.1-1.7) \times 10^9$ M^{-1} s^{-1} for the reactions of **N(1−3)** with the highly electrophilic carbocations **E(30,31)**$^+$ (Table 2), indicating that these reactions are entirely controlled by diffusion. The diffusion rate constants for the reactions of **N1** and **N2** with benzhydrylium ions in CH_2Cl_2 are thus slightly smaller than the rate constants determined for the reactions of the same nucleophiles with **E26**$^+$ in CH_3CN ($k_2 \approx 2.4 \times 10^9$ M^{-1} s^{-1}).[25] For the less nucleophilic compounds **N(4−16)**, the diffusion limit (plateau of log k_2 vs E correlations) could not be determined due to the lack of a method to generate sufficiently electrophilic carbocations.

For reactions of **N(1−3)** that proceed with rate constants $k_2 < 1 \times 10^8$ M^{-1} s^{-1}, there is an excellent agreement between the

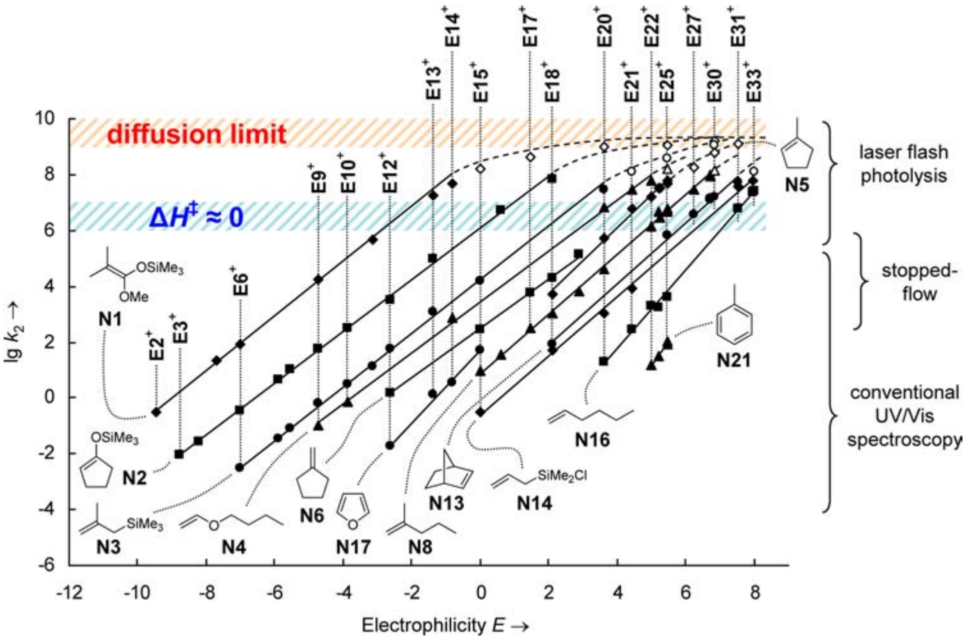


Figure 2. Plot of log k_2 versus E for the reactions of benzhydryl cations with π-nucleophiles. Open symbols indicate rate constants $k_2 > 10^8$ M^{-1} s^{-1}. For the sake of clarity, only selected data are shown; complete plots for all correlations are compiled in sections S3.4 and S3.5 of the Supporting Information. The blue-shaded area indicates the region where the activation enthalpy reaches the value $\Delta H^‡ = 0$ (see text).

experimental rate constants from the laser flash measurements (Table 2) and the rate constants calculated by eq 1 using the previously published E, N, and s_N parameters which were derived from reactions monitored by conventional and stopped-flow UV/vis spectrophotometry.[1b] On the other hand, the rate constants for the reactions of **N**(**1**−**3**) in the range of k_2 = (1−5) × 10^8 M^{-1} s^{-1} show substantially larger deviations from the values predicted by eq 1, which indicates that the limiting effect of diffusion is already noticeable in reactions with second-order rate constants $k_2 > 1 \times 10^8$ M^{-1} s^{-1}. Relative reactivities derived from product ratios in CH_2Cl_2 had previously led to the same conclusion.[14]

New Electrophilicity Parameters. *Data Set for the Correlation Analysis.* The directly measured rate constants for the reactions of **E**$^+$ with **N**(**1**−**3**) in CH_2Cl_2 which are presented in the preceding paragraphs confirm our previous practice to consider only rate constants $k_2 < 1.0 \times 10^8$ M^{-1} s^{-1} for the correlation analysis, as the correlation lines are flattening when this rate constant is exceeded.[1b] As reported before,[1b,c,26] solvent effects on the rates of the reactions of benzhydrylium ions with neutral π-nucleophiles are small. This can be derived from the good agreement between the rate constants for the reactions in CH_2Cl_2 (Table 2) and the rate constants that were previously published for some of these electrophile−nucleophile combinations in CH_3CN.[25] Although the differences between the two solvents are small (factor 1.2−5), the rate constants reported for CH_3CN are generally higher than those measured in CH_2Cl_2. As we can now also determine rate constants for fast reactions in CH_2Cl_2, i. e., in the same solvent which was employed for measuring the rate constants of the slower reactions ($k_2 < 10^6$ M^{-1} s^{-1}),[1b] we restricted the correlation analysis in this work to data acquired in CH_2Cl_2 (Table 2), and we excluded the data for reactions in acetonitrile which were included in the original correlation analysis.[1b]

The data determined by laser flash photolysis experiments in this work (Table 2) are supplemented by other previously reported[1b,15,18,22,23a,27] and newly determined (Table 2) rate constants for the reactions of benzhydryl cations **E**$^+$ with the π-nucleophiles **N**(**1**−**16**) in CH_2Cl_2 which were determined by conventional[26] or stopped-flow[1b] UV/vis spectroscopic measurements. Although we have not determined additional rate constants for the reactions of (E)-propenylbenzene (**N19**), m-xylene (**N20**), and toluene (**N21**), their N and s_N parameters were also subjected to the correlation analysis because they are linked to the electrophilicities of the benzhydrylium ions **E**(**21**−**23**,**25**,**26**)$^+$ ($E > 4$) which will be revised in this work.[28] A complete list of all rate constants used for the correlation analysis can be found in Table S3.1 in the Supporting Information.

Variables in the Correlation Analysis. One of the reasons why we selected benzhydrylium ions as reference electrophiles for deriving reactivity parameters of nucleophiles according to eq 1 was to avoid the need for a continuous reparametrization whenever we acquired reactivity parameters for previously uncharacterized compounds.[1b,g] In this work, we have gathered a large number of new rate constants for a series of benzhydrylium ions which have not yet belonged to the reference electrophiles (Table 2), and there is no reason for treating these data differently from those for other benzhydrylium ions. In addition, Table 2 lists 18 new rate constants k_2 for reactions of **E**(**21**,**23**,**25**,**26**)$^+$ with π-nucleophiles in CH_2Cl_2 at 20 °C which are below 10^8 M^{-1} s^{-1}. As the E parameters for these benzhydrylium ions had previously been derived from 14 rate constants determined in CH_2Cl_2 and 8 rate constants from laser flash photolysis experiments in CH_3CN,[1b] we have now revised the electrophilicity parameters of the four reference systems **E**(**21**,**23**,**25**,**26**)$^+$ using only the rate constants for their reactions with π-nucleophiles in CH_2Cl_2 (from Table 2 and refs 1b, 27).

In order to avoid insignificant changes of all previously published reactivity parameters for the sake of introducing some new systems and updating a small section ($E > 4$) of our electrophilicity scale ($-24 \le E \le 6$), we kept the E parameters of **E**(**1**−**13**)$^+$ and **E**(**15**−**20**)$^+$ fixed to the values obtained in the previous correlation (Table 1).[1b] Thus, the only variables in the correlation analysis were the E parameters of $\mathbf{E(21-33)^+}$ ($E > 4$) and of $\mathbf{E14^+}$ (not reported previously), as well as the reactivity parameters N and s_N of $\mathbf{N(4-21)}$ which were derived from the reactions of the corresponding nucleophiles with $\mathbf{E(21-33)^+}$. The N and s_N parameters of the overwhelming number of other nucleophiles are not affected by the new correlation analysis, because they were derived exclusively from the reactivities toward less reactive electrophiles with unchanged E parameters.[29]

Fixed points of our initial correlation were $E = 0.00$ for $\mathbf{E15^+}$ and $s_N = 1.00$ for **N8**.[1b] However, the inclusion of the rate constants listed in Table 2 in the correlation more than doubles the number of available rate constants for **N8**, which now adopts a value of $s_N = 1.06$. In order to avoid extensive changes of published reactivity parameters, the slopes of the correlations are now defined by reactions of allyltrimethylsilane (**N7**; $s_N = 1.00$).[30]

Correlation Analysis. In analogy to our previous treatment,[1b] the E parameters of $\mathbf{E(21-33)^+}$ and $\mathbf{E14^+}$ and the N and s_N parameters of $\mathbf{N(4-21)}$ were calculated by a least-squares minimization. For that purpose, we minimized Δ^2 specified by eq 2 using the nonlinear solver program "What'sBest! 7.0 Industrial" by Lindo Systems Inc.[31] with the constraints that were discussed in the previous section.

$$\Delta^2 = \sum (\log k_2 - \log k_{\text{calc}})^2 = \sum (\log k_2 - s_N(N + E))^2 \qquad (2)$$

A total of 116 rate constants for the reactions of 14 benzhydrylium ions with 19 π-nucleophiles were employed for this correlation analysis (see Table S3.1 in the Supporting Information). Tables 2 and S3.1 provide a comparison of the calculated rate constants k_{calc} obtained in this manner with the experimental values k_2. The quality of the new correlation (standard deviation as defined in ref 1b: $\sigma = 1.36$) is slightly poorer than that of the previous correlation analysis ($\sigma = 1.19$).[1b] The larger deviations may be due to the incorporation of more reactions with rate constants $k_2 > 10^7$ M^{-1} s^{-1} and of more reactions for which the rate constants k_2(20 °C) were extrapolated from measurements at lower temperatures. These reactions also showed larger deviations in the previous correlation analysis.[1b] Still, for 112 out of 116 reactions, the deviations between k_{calc} and k_{exp} are within the range observed in the previous analysis (deviation ≤ factor 1.7).[1b]

Figure 2 illustrates the correlations by plotting log k_2 for the reactions of $\mathbf{E^+}$ with **N** against the E parameters of the benzhydrylium ions. The figure also shows the good agreement of experimental (filled symbols) and calculated (lines) rate constants for the reactions of $\mathbf{E^+}$ with $\mathbf{N(1-3)}$, whose N and s_N parameters were kept fixed in the correlation analysis. As discussed above, deviations from linearity are observed for reactions with $k_2 > 10^8$ M^{-1} s^{-1}, and these rate constants (open symbols) were excluded from the calculation of the E, N, and s_N parameters. The excellent linear correlations for reactions with $k_2 < 10^8$ M^{-1} s^{-1} demonstrate the agreement of the different kinetic methods employed to measure the rate constants. These methods include conventional UV/vis spectrophotometry at 20 °C, extrapolation of k_2(20 °C) from conventional UV/vis spectrophotometry at lower temperatures, stopped-flow UV/vis spectrophotometry (20 °C), and laser flash photolysis measurements (20 °C) from this work.

For the sake of clarity, not all correlations are shown in Figure 2, and several rate constants $k_2 > 10^8$ M^{-1} s^{-1} are omitted. Complete plots of log k_2 versus E for all nucleophiles **N** are compiled in section S3.4 of the Supporting Information. Equation 1 requires linear correlations with slopes of unity for plots of (log k_2)/s_N versus N. Such plots are shown for all electrophiles $\mathbf{E^+}$ in section S3.5 of the Supporting Information, and the readers may convince themselves that the optimized slopes are indeed close to unity ($s_E = 1.00 \pm 0.14$).

The electrophilicity parameters E of $\mathbf{E(21-33)^+}$ and $\mathbf{E14^+}$ obtained from the new correlation analysis are summarized in Table 1. The values for $\mathbf{E(21-23)^+}$ and $\mathbf{E(25,26)^+}$ are 0.2–0.5 unit smaller than the previously published values.[1b] Calculations based on the new values will yield rate constants that deviate by less than a factor of 3.5 from those obtained with the old E parameters. The largest change is found for $\mathbf{E26^+}$ ($E = 5.48$), which can be rationalized by the fact that the previously published value of $E = 6.02$ for $\mathbf{E26^+}$ was mostly based on reactions in CH_3CN, which are somewhat faster than in CH_2Cl_2 (see above).

Since only one or two rate constants $k_2 < 10^8$ M^{-1} s^{-1} are available for the most electrophilic benzhydrylium ions $\mathbf{E32^+}$ and $\mathbf{E33^+}$, their E parameters have to be considered approximate. Although rate constants $k_2 > 1.0 \times 10^8$ M^{-1} s^{-1} were not considered in the correlation analysis, the data in Table 2 show that in many cases eq 1 also provides good estimates for reactions with rate constants in the range of (1.0–2.0) × 10^8 M^{-1} s^{-1} or only slightly overestimates the rate constants of such reactions. The good agreement between k_{calc} and k_2 for reactions of $\mathbf{E32^+}$ and $\mathbf{E33^+}$ with rate constants $k_2 < 2.0 \times 10^8$ M^{-1} s^{-1} thus substantiates the electrophilicity parameters of $E = 7.96$ for $\mathbf{E32^+}$ and $E = 8.02$ for $\mathbf{E33^+}$ that were derived from the few available rate constants $k_2 < 1.0 \times 10^8$ M^{-1} s^{-1}.

Figure 3 illustrates that the substituent effects of the m-F and p-CF_3 groups on the electrophilicities of the benzhydrylium ions $\mathbf{E^+}$ are additive: Each p-CF_3 substituent increases the E value by 1.2 units and each m-F substituent by ~0.7 unit. A comparison of the E parameters of $\mathbf{E24^+}$ and $\mathbf{E20^+}$ shows a similar increment of $\Delta E = 0.8$ per m-F substituent. Additivity of the m-F-effects has also been reported for the electrophilicities E of tritylium ions[32a] and the electrofugalities E_f of benzhydrylium[20] and tritylium ions.[32b] In contrast, the effects

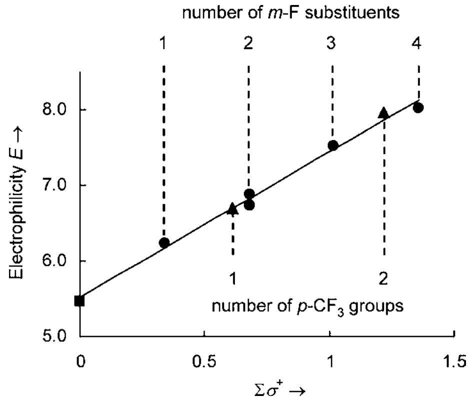


Figure 3. Plot of the E parameters for the parent (■), m-F-substituted (●), and p-CF_3-substituted (▲) benzhydrylium ions $\mathbf{E(25)^+}$ and $\mathbf{E(27-33)^+}$ against the sum of the σ^+ parameters of their substituents (linear fit: $E = 1.92\sigma^+ + 5.52$, $R^2 = 0.9927$, $n = 8$).

of donor substitutents have generally been found to be nonadditive (saturation effect).[1b,4]

Free Energy Relationships. As shown in Figure 2, all rate constants $k_2 < 10^8$ M^{-1} s^{-1} correlate linearly with E, and curvature is only observed for $k_2 > 10^8$ M^{-1} s^{-1} as the diffusion limit is approached. In previous work, we had determined activation parameters for the reactions of benzhydrylium ions with olefins in CH_2Cl_2.[1b,27] Typically, variation of the electrophiles only affected the activation enthalpy $\Delta H^‡$ while the activation entropy $\Delta S^‡$ remained constant within experimental error for reactions with rate constants in the range $10^{-2} < k_2 < 5 \times 10^4$ M^{-1} s^{-1}.[33] Figure 4 (open symbols) illustrates this behavior for reactions of benzhydrylium ions with allyltrimethylsilane (**N7**) and 2-methylpent-1-ene (**N8**).

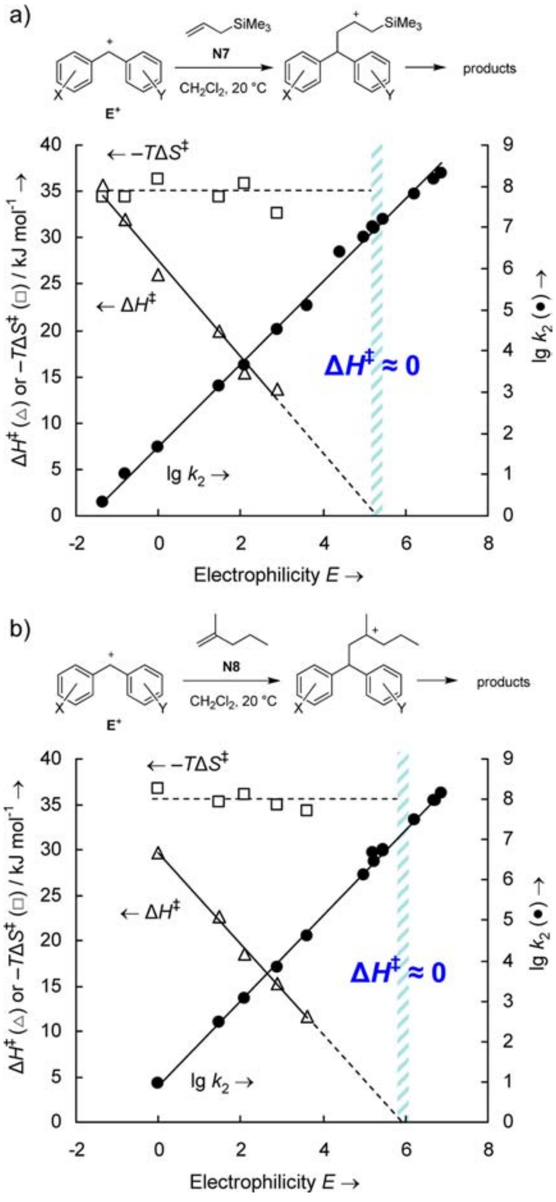


Figure 4. Correlations between the activation parameters $\Delta H^‡$ (Δ) and $-T\Delta S^‡$ (□) for the reactions of benzhydrylium ions E^+ with (a) allyltrimethylsilane and (b) 2-methylpent-1-ene and the electrophilicity parameters E of the benzhydrylium ions. The correlations of log k_2 (●) versus E remain linear well beyond the extrapolation to $\Delta H^‡ = 0$.

Extrapolation of the correlation lines, as indicated by the dashed lines in Figure 4, showed that for the investigated reactions $\Delta H^‡$ might become 0 for carbocations of E = 5−6, and the question arose whether the rate constants would grow further when more electrophilic carbocations are employed. As it was not possible at that time (1995) to generate more electrophilic carbocations laser-flash-photolytically in CH_2Cl_2 solution (only investigations in CH_3CN were possible), we approached this question indirectly. From competition experiments with π-systems of different reactivity, we concluded that crossing the point $\Delta H^‡ = 0$ is not associated with a bend of the linear free energy relationship and that $\Delta S^‡$ starts changing as $\Delta H^‡$ becomes zero.[33]

Using the recently introduced method to generate highly reactive carbocations in CH_2Cl_2 solution from benzhydryl triarylphosphonium salts with complex counterions,[18] we have now been able to study also rates of the reactions of highly reactive carbocations with olefins in CH_2Cl_2, as listed in Table 2. Figure 4 shows that the correlation log k_2 versus E does not experience a break when the extrapolated correlation line $\Delta H^‡$ vs E arrives at $\Delta H^‡ = 0$.

Table S4.1 in the Supporting Information summarizes previously determined activation parameters for the reactions of **N7** and **N8** with benzhydrylium ions in CH_2Cl_2. For these and other structurally related nucleophiles,[1b,27] we typically found activation entropies $\Delta S^‡$ in between −110 and −130 J mol^{-1} K^{-1} which correspond to second-order rate constants of $k_2 = (1{-}10) \times 10^6$ M^{-1} s^{-1} for $\Delta H^‡ = 0$. Figure 2, where this range of rate constants is marked by a light-blue shading, shows that all correlation lines cross this range without noticeable bending. Bending only occurs for $k_2 > 10^8$ M^{-1} s^{-1} when the diffusion limit is approached.

Kinetics of the Reactions of Benzhydrylium Ions with Other Classes of Nucleophiles. In the previous sections we have derived electrophilicity parameters for the acceptor-substituted benzhydrylium ions $\mathbf{E(27{-}33)^+}$ from the rate constants of their reactions with π-nucleophiles in CH_2Cl_2. In the subsequent sections we will examine the applicability of these E parameters to other types of reactions such as reactions of benzhydrylium ions with hydride donors[1b,34] and solvents.[16,35−37]

Triethylsilane in CH_2Cl_2. The second-order rate constants k_2 (M^{-1} s^{-1}) for the reactions of benzhydrylium ions $\mathbf{E}^+$ with the hydride donor triethylsilane (**N22**) in CH_2Cl_2 at 20 °C, which are listed in Table 3, were determined in the same manner as described above for the π-nucleophiles. Figure 5a shows an excellent linear correlation of these rate constants with the electrophilicity parameters E of the benzhydrylium ions. From this correlation, we obtained the nucleophilicity parameters N = 3.58 and s_N = 0.70 for **N22**, in good agreement with the previously reported values (N = 3.64, s_N = 0.65)[1b] that were based on only two rate constants.

Trifluoroethanol. Equation 1 can also predict first-order rate constants k_1 (s^{-1}) for reactions of carbocations with solvents when the solvent-specific nucleophilicity paramters N_1 and s_N are employed.[35] It was shown, for example, that the first-order rate constants k_1 for the decay of benzhydrylium ions $\mathbf{E}^+$ in 2,2,2-trifluoroethanol correlate with the E parameters of $\mathbf{E}^+$.[35] Because trifluoroethanol stabilizes anions very well, the recombination reactions of the photofragments proceed with negligible rates when anionic photoleaving groups such as acetate or p-cyanophenolate are employed. Using this method, McClelland and Steenken were able to determine rate

Table 3. Second-Order Rate Constants k_2 for the Reactions of Electrophiles E^+ with Triethylsilane (N22)[a] in CH_2Cl_2 at 20 °C and Comparison with Rate Constants k_{calc} Calculated from Equation 1

E^+	electrophile abbreviation	E	k_2/ M^{-1} s^{-1}	k_{calc}[b]/ M^{-1} s^{-1}	k_{calc}/k_2
E13$^+$	$(fur)_2CH^+$	−1.36	3.76×10^{1}[c]	3.58×10^{1}	0.95
E14$^+$	fur(ani)CH^+	−0.81	7.94×10^{1}[d]	8.69×10^{1}	1.09
E15$^+$	$(ani)_2CH^+$	0.00	3.98×10^{2}[c]	3.21×10^{2}	0.81
E17$^+$	ani(tol)CH^+	1.48	4.87×10^{3}[c]	3.48×10^{3}	0.72
E18$^+$	ani(Ph)CH^+	2.11	5.29×10^{3}[e]	9.62×10^{3}	1.82
E27$^+$	mfp(Ph)CH^+	6.23	6.66×10^{6}[f]	7.36×10^{6}	1.11
E30$^+$	$(mfp)_2CH^+$	6.87	2.51×10^{7}[f]	2.07×10^{7}	0.82
E31$^+$	dfp(mfp)CH^+	7.52	6.04×10^{7}[f]	5.89×10^{7}	0.97

[a] Nucleophile **N22**, formula = H-$SiEt_3$, N = 3.58, s_N = 0.70. [b] Calculated from eq 1. [c] Stopped-flow UV/vis measurement, from ref 23b. [d] Conventional UV/vis spectrophotometry, from ref 23a. [e] Conventional UV/vis spectrophotometry, from ref 1b. [f] Laser flash photolysis of triarylphosphonium salts, this work.

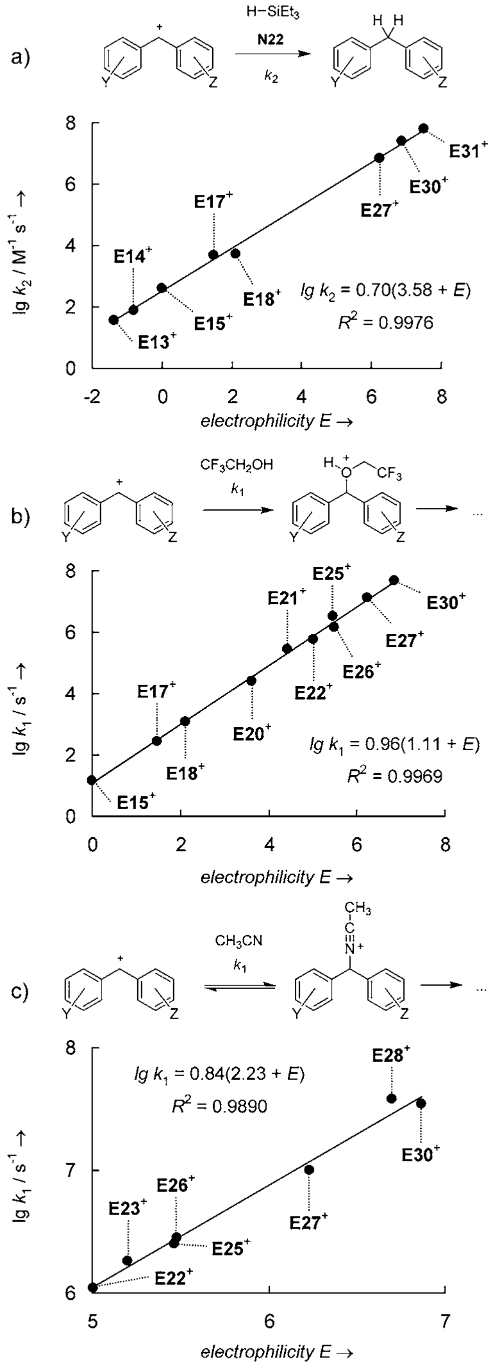


Figure 5. Plots of log k_2 or log k_1 for reactions of benzhydrylium ions $\mathbf{E}^+$ with triethylsilane (a), 2,2,2-trifluoroethanol (b), and acetonitrile (c) versus the E parameters of $\mathbf{E}^+$.

constants in the range $1 \times 10^1 < k_1 < 4 \times 10^6$ s^{-1} for the first-order decay reactions of the benzhydrylium ions **E(15,17,18,20,21,25)**$^+$ in trifluoroethanol.[37] Figure 5b illustrates that the rate constants for the reactions of **E22**$^+$, **E26**$^+$, **E27**$^+$, and **E30**$^+$ with trifluoroethanol[18] nicely extend the correlation line and thus confirm the consistency of the E values determined in this work. The reactivity parameters of trifluoroethanol obtained from Figure 5b, N_1 = 1.11 and s_N = 0.96, are close to the previously reported values (N_1 = 1.23, s_N = 0.92).[35]

Acetonitrile. The formation of nitrilium ions from carbenium ions and nitriles is a key step in the Ritter reaction.[38,39] In dry CH_3CN (≤2 mM H_2O), photolytically generated benzhydrylium ions ($\mathbf{E}^+$) with $E \geq 5$ were reported to decay via formation of nitrilium ions **E**-$N^+{\equiv}C{-}CH_3$, which are subsequently hydrolyzed to *N*-(diarylmethyl)acetamides **E**-NHC(O)CH_3.[40] Photolytically generated benzhydrylium ions with $E < 5$ show nonexponential decay kinetics in CH_3CN due to the recombination of $\mathbf{E}^+$ with the photoleaving group.[18,40] Therefore, the reactions of CH_3CN with these benzhydrylium ions cannot be followed with the laser flash photolysis technique.

The previously reported first-order rate constants for the decays of the highly electrophilic benzhydrylium ions **E(22−30)**$^+$ in anhydrous acetonitrile[18,40] that proceed via formation of the nitrilium ions **E**-$N^+{\equiv}C{-}CH_3$ can now be correlated with the electrophilicity parameters E of the benzhydrylium ions $\mathbf{E}^+$ from this work to characterize the solvent nucleophilicity of acetonitrile (Figure 5c). The resulting solvent nucleophilicity parameters for acetonitrile, N_1 = 2.23 and s_N = 0.84, are comparable to those of trifluoroethanol. As **E15**$^+BF_4^-$ (E = 0.00) can be dissolved in CH_3CN to give a persistent solution despite a calculated rate constant of 74.7 s^{-1} ($\tau_{1/2}$ < 10 ms) for its reaction with CH_3CN, one can conclude that CH_3CN is a weak Lewis base and its reaction with **E15**$^+$ is highly reversible.

■ CONCLUSION

Second-order rate constants for the reactions of the benzhydrylium ions **E(13−33)**$^+$ with π-nucleophiles in CH_2Cl_2 could be determined using benzhydryl triarylphosphonium salts as precursors for the laser flash photolytic generation of these carbocations.[18] In this way, it became possible to determine electrophilicity parameters E for the highly reactive acceptor-substituted benzhydrylium ions **E(27−33)**$^+$, which have previously not been accessible by laser flash photolysis.[16] The consistency of the newly determined E values was demonstrated by showing that the electrophilicity parameters derived from reactions with π-nucleophiles are also applicable to reactions of these carbenium ions with other types of nucleophiles, such as triethylsilane, acetonitrile, or trifluoroethanol. This study thus presents an extension of our electrophilicity scale to the more reactive carbocations **E(27−33)**$^+$, which will be employed in subsequent work to characterize the reactivities of further weak nucleophiles.

Most remarkable is that, in all series investigated, the linear correlations of log k_2 versus E do not show any bending over the entire range of rate constants from 10^{-4} to 10^{8} M^{-1} s^{-1}, although this range encompasses reaction series with widely differing transition states, and leveling only occurs for $k_2 > 10^8$ M^{-1} s^{-1}, when the diffusion limit $[(1.1-1.7) \times 10^9$ M^{-1} s^{-1} in $CH_2Cl_2]$ is approached. Figure 4 shows that in slow reactions $(10^{-4} < k_2 < 5 \times 10^4$ M^{-1} $s^{-1})$ of **N7** or **N8** with the alkoxy- and methyl-substituted benzhydrylium ions **E(13−20)**$^+$, variation of the benzhydrylium ions exclusively changes the activation enthalpies $\Delta H^{\ddagger}$ while the activation entropies $\Delta S^{\ddagger}$ remain almost constant. One can extrapolate that $\Delta H^{\ddagger}$ will disappear for reactions with $k_2 > (1-10) \times 10^6$ M^{-1} s^{-1}. Despite the fact that such fast reactions correspond to processes which proceed only downhill on a potential energy surface, log k_2 continues to increase linearly with E. We are not aware of any other reaction series, where linear free energy relationships extend over such wide ranges, and only bend when the observed reaction constants exceed 10^8 M^{-1} s^{-1}, i.e., get close to the diffusion rate constants.

The observation that, in all reaction series investigated, variation of a carbocation has exactly the same effect on the rate constants of enthalpy-controlled reactions as on rate constants of reactions where the reactants slide into each other without crossing an enthalpy barrier is of fundamental importance for our understanding of chemical reactivity. Though proportional changes of $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ have long been known (compensation effect),[41] it is most surprising that the linearity of linear free energy relationships persists in the range of activation-less reactions, which challenges theoretical treatments.

■ ASSOCIATED CONTENT

Supporting Information

Details of the kinetic experiments and the correlation analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

Herbert.Mayr@cup.uni-muenchen.de

Notes

The authors declare no competing financial interest.

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(28) The revised reactivity parameters for these nucleophiles are: $N = -0.49$, $s_N = 1.18$ for (*E*)-propenylbenzene (**N19**); $N = -3.57$, $s_N = 2.08$ for *m*-xylene (**N20**); and $N = -4.36$, $s_N = 1.77$ for toluene (**N21**). See Supporting Information for details.

(29) The N and s_N parameters of **N17** and **N18**, however, are also revised in this work because the previous values were based on only three rate constants for reactions of each of these nucleophiles with reference electrophiles.

(30) We are aware of the fact that this is not strictly correct, because slightly different reactivity parameters would result if we subjected all E, N, and s_N parameters to a correlation analysis with fixed values only for **E15**$^+$ ($E = 0.00$) and **N7** ($s_N = 1.00$). The inconsistencies introduced by this procedure are negligible, but in this way we can update some reactivity parameters without changing all previously published values.

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