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Why are Vinyl Cations Sluggish Electrophiles?

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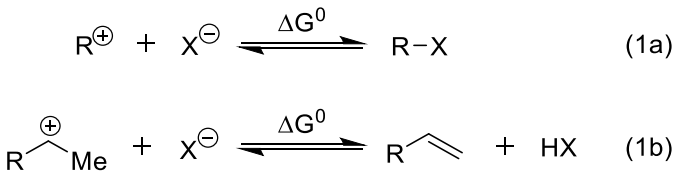
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Abstract. The kinetics of the reactions of the vinyl cations **2** [$Ph_2C{=}C^+$-(4-MeO-C_6H_4)] and **3** [$Me_2C{=}C^+$-(4-MeO-C_6H_4)] (generated by laser flash photolysis) with diverse nucleophiles (e.g. pyrroles, halide ions, alcoholic and aqueous solvents) have been determined photometrically. It was found that the reactivity order of the nucleophiles toward these vinyl cations is the same as that towards diarylcarbenium ions (benzhydrylium ions). However, the reaction rates of vinyl cations are affected only half as much by variation of the nucleophiles as those of the benzhydrylium ions. For that reason, the relative reactivities of vinyl cations and benzhydrylium ions depend strongly on the nature of the nucleophiles. It is shown that vinyl cations **2** and **3** react, respectively, 227 and 14 times more slowly with trifluoroethanol than the parent benzhydrylium ion $(Ph)_2CH^+$, even though in solvolysis reactions (80 % aqueous ethanol at 25 °C) the vinyl bromides leading to **2** and **3** ionize much more slowly (half-lives 1.15 yrs and 33 days) than $(Ph)_2CH$-Br (half-life 23 s). The origin of this counter-intuitive phenomenon was investigated by high-level MO calculations. We report that vinyl cations are not exceptionally high energy intermediates, and that high intrinsic barriers for the $sp^2 \rightleftharpoons sp$ rehybridizations account for the general phenomenon that vinyl cations are formed slowly by solvolytic cleavage of vinyl derivatives, and are also consumed slowly by reactions with nucleophiles.

Introduction

Over the course of the last century, the properties of carbocations (which frequently are reactive intermediates) have been investigated by diverse techniques in order to understand their role in organic chemical reactions.[1,2,3,4,5,6,7,8,9,10,11] Although there exist several means for quantifying the stabilities of carbocations in solution and in the gas phase,[2-10,12,13] general stability scales for carbocations (R^+) do not exist, i.e., the absolute stability of a given carbocation cannot be uniquely defined.[2,14] Frequently, the equilibrium constants of their reactions with a certain reference Lewis base X^- (eq. 1a), i.e. their Lewis acidities with respect to X^-, are employed as a measure of their relative stabilities.[2-9,12,15,16,17] Alternatively, carbocations have been ranked

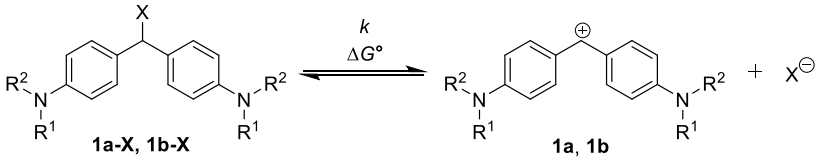
according to their Brønsted acidities with respect to a certain Brønsted base (eq. 1b),[2b,18] and most Brønsted acidity scales refer to the reaction medium (solvent) as the reference base.



Solvolysis reactions often proceed with rate-determining heterolytic cleavage of R-X (reverse of reaction 1a). The initially formed intermediate carbocation R^+ is then immediately trapped by the solvent and does not recombine with the leaving group.[1,19] As the transition state of this cleavage is generally assumed to be carbocation-like (Hammond's postulate), the rates of the solvolysis reactions of R-X have frequently been considered to be a measure for the relative stabilities of the intermediate carbocations.[1,6c]

In several series of solvolysis reactions, linear relationships between the measured solvolysis rates and the Lewis acidities of the intermediate carbocations (which are derived from equilibrium measurements) have been observed, but deviations from such rate-equilibrium relationships have also been reported.[12,15,20,21,22] In our investigations of the reactivities of benzhydryl derivatives, we have observed, for example, that benzhydrylium ion **1a** is formed 22 times faster than **1b** during solvolysis of the corresponding benzoates (Scheme 1)[20] even though **1a** is the stronger Lewis acid according to equilibrium studies in solution and computational studies for the gas phase (Scheme 1).[12,15]

Scheme 1. Rate constants (k) and Gibbs energies of reaction ($\Delta G°$) for heterolysis reactions giving benzhydrylium ions **1a** and **1b**.



X =	**1a-X** $R^1 = CH_2CF_3$, R^2 = Me	**1b-X** R^1 = Ph, R^2 = Ph
$PhCO_2$	k = 6.06 × 10^{-2} s^{-1} [a]	k = 2.79 × 10^{-3} s^{-1} [a]
$PhCO_2$	$\Delta G°$ = 16.2 kcal mol^{-1} [b]	$\Delta G°$ = 15.7 kcal mol^{-1} [b]
CH_3	$\Delta G°$ = 170.0 kcal mol^{-1} [c]	$\Delta G°$ = 164.8 kcal mol^{-1} [c]

[a] Experimental rate constant for reaction at 25 °C in 80:20 MeCN/H_2O.[20]

[b] Gibbs reaction energy $\Delta G°$ at 20 °C calculated using lg $K = LA + LB$,[12] in which the LA values of **1a** and **1b** in CH_2Cl_2 (−5.39 and −5.72, respectively), and the LB value of benzoate in MeCN (17.45) were employed.

[c] Negative of the calculated gas phase methyl anion affinity of the benzhydrylium ion at 20 °C (see reference 15).

What is the origin of this discrepancy? Direct rate measurements in the solvents used for the solvolysis studies showed that most flash photolytically generated benzhydryl cations react

with chloride and bromide ions under diffusion control.[19] As there is obviously no barrier for the ion combination, one can conclude that in the reverse reaction (first step of an S_N1 reaction) the transition state also corresponds to the ion pair (Figure 1).

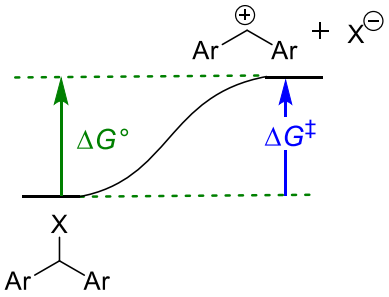


Figure 1. First step of the S_N1 reaction of a benzhydryl halide giving benzhydrylium ion and halide anion.

On the other hand, we have measured significant barriers for the combinations of benzhydrylium ions with carboxylate anions (as depicted for the reactions from right to left in Figure 2).[21] From the principle of microscopic reversibility one can now derive that the first step of an S_N1 reaction of a benzhydryl carboxylate also must proceed via a transition state that is higher in energy than the carbocation (see reactions from left to right in Figure 2).

According to Marcus (eq. 2),[23a-g] the Gibbs activation energy ($\Delta G^{\ddagger}$) of a chemical reaction can be expressed by a combination of the Gibbs reaction energy ($\Delta G°$) and the intrinsic barrier ($\Delta G^{\ddagger}_0$), the latter of which corresponds to $\Delta G^{\ddagger}$ for an identity reaction. For reaction series where identity reactions cannot be established, e.g. carbocation-anion combinations, the intrinsic barrier $\Delta G^{\ddagger}_0$ is commonly obtained by extrapolations to reactions with $\Delta G° = 0$.[23h]

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \frac{\Delta G°}{2} + \frac{(\Delta G°)^2}{16\Delta G_0^{\ddagger}} \qquad (2)$$

Consider two heterolysis reactions, involving different species A-X and B-X, that have identical Gibbs energies of reaction ($\Delta G°$) but different Gibbs energies of activation ($\Delta G^{\ddagger}$(A) < $\Delta G^{\ddagger}$(B)), as shown in Figure 2. Since the thermodynamic contribution ($\Delta G°$) to the Gibbs energy of activation in both cases is identical, the difference between $\Delta G^{\ddagger}$(A) and $\Delta G^{\ddagger}$(B) must arise exclusively from the differences between the intrinsic barriers $\Delta G^{\ddagger}_0$(A) and $\Delta G^{\ddagger}_0$(B) (not shown explicitly in Figure 2). Thus, in the case depicted in Figure 2, the intrinsic barrier $\Delta G^{\ddagger}_0$(B) must be greater than $\Delta G^{\ddagger}_0$(A). The energy profiles in Figure 2 now illustrate the counterintuitive conclusion that in cases where the difference of the heterolysis rates is mostly due to a difference in intrinsic barriers, the carbocation that is formed more quickly, A^+, also reacts more quickly than B^+ with X^-.

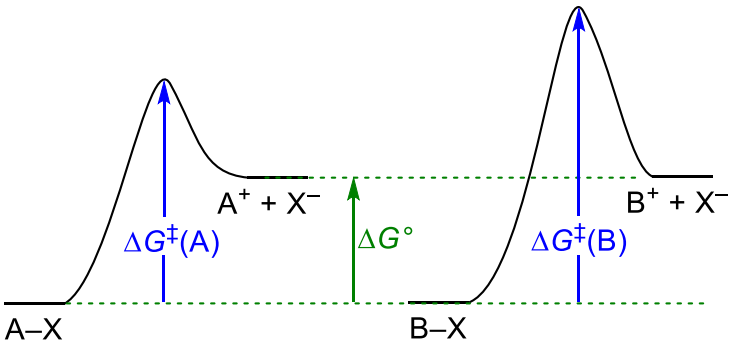


Figure 2. Comparison of ionizations of the alkyl halides A-X and B-X to give carbocations A^+ and B^+ of equal Lewis acidity with different rates.

Let us now return to the example illustrated in Scheme 1. As the Lewis acidity of carbocation **1a** is slightly higher than that of **1b**, the higher solvolysis rate of **1a-X** compared to **1b-X** must be due to the lower intrinsic barrier for the ionization of **1a-X** than of **1b-X**. With this conclusion, we can explain why carbocation **1a**, which is formed faster in S_N1 reactions than **1b**, has also been found to generally react faster with nucleophiles than **1b**.[24]

What is the consequence of these considerations for vinyl cation chemistry? The very low S_N1 reactivities of vinyl halides and vinyl tosylates[25,26,27] have commonly been ascribed to low thermodynamic stabilities of vinyl cations due to the sp-hybridization of the carbenium center.[28,29] However, when one considers that the 1-phenylvinyl cation has a similar hydride affinity to the benzyl cation,[30,31,32] only 2.9 kcal mol^{-1} greater than that of the *tert*-butyl cation,[30] the question arises whether the low solvolysis rates of vinyl halides are really mostly due to the low thermodynamic stabilities of dicoordinated carbenium ions. If instead high intrinsic barriers for the $sp^2 \rightleftharpoons sp$ rehybridization were responsible for the slow solvolyses of vinyl derivatives, the discussion of Figure 2 implies that also the reverse reaction should be slow, and vinyl cations should not be extraordinarily reactive intermediates but rather sluggish electrophiles. Though rate constants for the reactions of vinyl cations generated by laser-flash photolysis with a variety of nucleophiles have previously been reported,[33,34] a systematic comparison of the electrophilic reactivities of vinyl cations and tricoordinated carbenium ions has not yet been performed. We now report on a systematic analysis of the reactivities of vinyl cations and show that exceptionally high intrinsic barriers account for their extraordinarily slow formation in S_N1 reactions as well as for their slow reactions with nucleophiles.

Results

Vinyl cations **2** and **3** (Chart 1), which can be generated by laser flash photolysis from **4-Br** and **5-Br**, were selected as representative vinyl cations to study the rates of the reactions with

nucleophiles **6**-**22** (Table 1) in MeCN (**13** and **14** in 2,2,2-trifluoroethanol, TFE) and with the solvent mixtures **23**-**41** listed in Table 2.

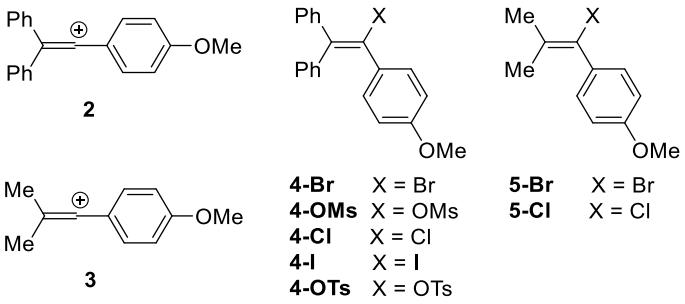
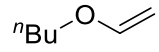
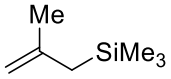
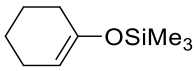
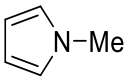
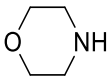
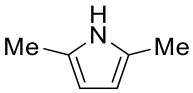
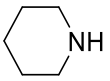
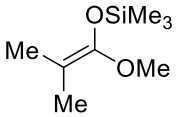
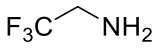


Chart 1. Structures of vinyl cations **2** and **3** and vinyl derivatives **4**-**X** and **5**-**X**.

Table 1. Structures and values of the nucleophile-specific parameters *N* and s_N (in MeCN unless otherwise indicated) for nucleophiles **6**-**22**.

Nucleophile	#	*N*	s_N	Ref	Nucleophile	#	*N*	s_N	Ref
	**6**	3.76	0.91	35	$^{t}BuNH_2$	**15**	12.35	0.72	37
	**7**	4.41	0.96	24	$^{i}PrNH_2$	**16**	13.77	0.70	37
	**8**	5.21	1.00	24	Et_2NH	**17**	15.10	0.73	37
	**9**	5.85	1.03	36		**18**	15.65	0.74	37
	**10**	8.01	0.96	36		**19**	17.35	0.68	37
	**11**	9.11	0.88	24	$^{n}Bu_4N^{\oplus}\,^{\ominus}OAc$	**20**	16.90	0.75	21
	**12**	10.13	0.75	37	$^{n}Bu_4N^{\oplus}\,^{\ominus}OMs$	**21**	-	-	-
$^{n}Bu_4N^{\oplus}\,^{\ominus}Cl$	**13**	10.3 [a]	0.60	19	$^{n}Bu_4N^{\oplus}\,^{\ominus}I$	**22**	-	-	-
$^{n}Bu_4N^{\oplus}\,^{\ominus}Br$	**14**	11.7 [a]	0.60	19					

[a] Solvent = 2,2,2-trifluoroethanol (TFE).

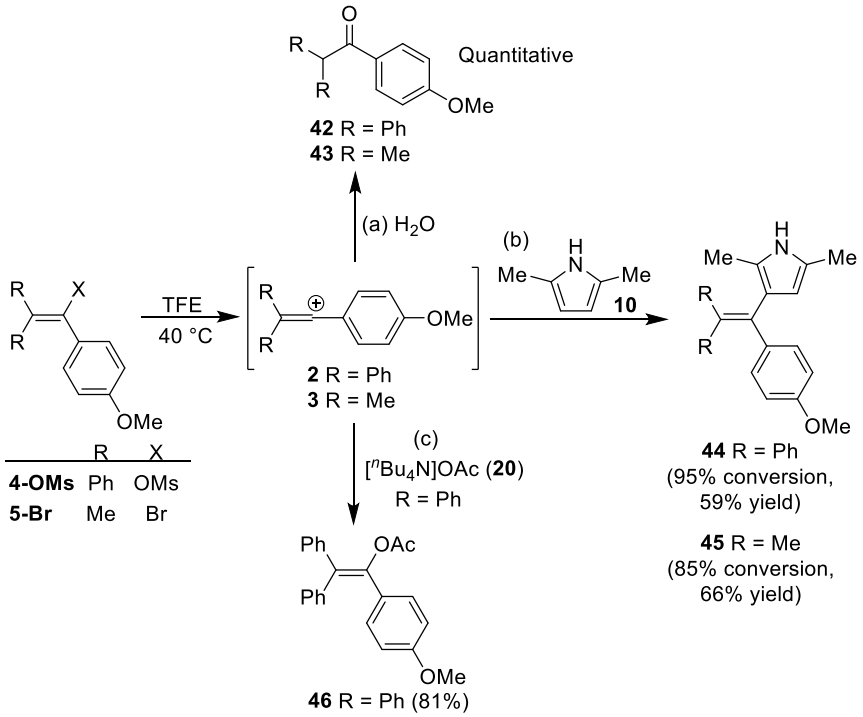
Table 2. Nucleophile-specific reactivity parameters N_1 and s_N for solvents and solvent mixtures (v/v) **23-41**.[38]

Nucleophile		N_1	s_N
TFE [a]	**23**	1.11 [a]	0.96 [a]
TFE/H_2O (90:10)	**24**	2.93	0.88
TFE/H_2O (60:40)	**25**	3.42	0.90
MeCN/H_2O (90:10)	**26**	4.56	0.94
MeCN/H_2O (80:20)	**27**	5.02	0.89
MeCN/H_2O (67:33)	**28**	5.02	0.90
MeCN/H_2O (50:50)	**29**	5.05	0.89
MeCN/EtOH (90:10)	**30**	5.19	0.96
MeCN/EtOH (80:20)	**31**	5.77	0.92
MeCN/EtOH (67:33)	**32**	6.06	0.90
MeCN/EtOH (50:50)	**33**	6.37	0.90
MeCN/EtOH (33:67)	**34**	6.74	0.89
MeCN/EtOH (20:80)	**35**	6.94	0.90
MeCN/EtOH (10:90)	**36**	7.10	0.90
EtOH/H_2O (40:60)	**37**	5.81	0.90
EtOH/H_2O (50:50)	**38**	5.96	0.89
EtOH/H_2O (60:40)	**39**	6.28	0.87
EtOH/H_2O (80:20)	**40**	6.68	0.85
EtOH/H_2O (90:10)	**41**	7.03	0.86

[a] TFE = 2,2,2-trifluoroethanol; N_1 and s_N are taken from ref 35.

Product Characterization

Scheme 2. Reactions of vinyl cations **2** and **3**, generated by ionization of **4-OMs** and **5-Br**, respectively, in TFE in the presence of different nucleophiles.



Vinyl cations **2** and **3** can be transiently generated in solvents of high ionizing power by heterolysis of precursor vinyl halides or pseudohalides **4**-X and **5**-X.[25,27,39,40a,41] We have found that heterolyses of **4-OMs** and **5-Br** occur at convenient rates at 40 °C in 2,2,2-trifluoroethanol (TFE), a solvent of low nucleophilicity (N_1 = 1.11).[35] When the vinyl cations are generated in aqueous TFE, the ketones **42** and **43** are formed quantitatively, as shown in Scheme 2a.

In order to verify that the vinyl cations generated in TFE solution can also be intercepted by other nucleophiles, **4-OMs** and **5-Br** were dissolved in TFE containing ≥ 1 mol L^{-1} of **10** or **20** as representative nucleophiles. Following our previously published methodology for carrying out Friedel-Crafts-type chemistry in neutral aqueous or alcoholic solutions,[42] high nucleophile concentrations were employed to avoid trapping by trifluoroethanol or traces of water. In this way, the reactions of solvolytically generated **2** and **3** with pyrrole **10** (N = 8.01 in MeCN) resulted in high conversion to 3-vinylpyrroles **44** and **45**, respectively (Scheme 2b), without formation of hydrolysis products.[43] The reaction of **2** with [^{n}Bu$_4$N]OAc (**20**; N = 16.9 in MeCN) gave vinyl acetate **46** (Scheme 2c) as the major product, with the formation of a small amount (5%) of hydrolysis product **42**.

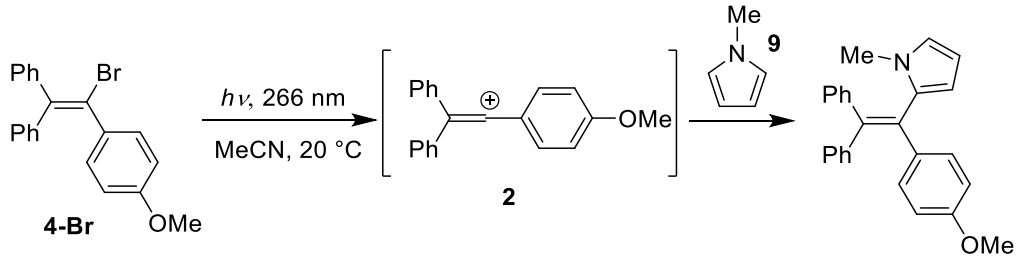
ipso-Substitution (at C-4 of the anisyl group), which has been observed in reactions of photochemically generated vinyl cations **2** with cyanide or alkoxide,[44,45] but not with alcohols,[45e,f] did not occur under the conditions described in Scheme 2. We therefore conclude,

that all nucleophiles added to the cationic sp-center of **2** and **3** in our kinetic experiments, in line with results from earlier studies carried out under similar conditions.[33,34,39,40,45e,45f,46,47,48,49]

Kinetic Investigations

Vinyl cations **2** and **3** were generated in MeCN, 2,2,2-trifluoroethanol, or solvent mixtures (Tables 1 and 2) by irradiation of the precursor vinyl bromides **4-Br** and **5-Br** with a 7-ns laser pulse of λ = 266 nm. A single signal is observed in the UV-Vis spectrum of each transient cation.[50] In the presence of a large excess of the nucleophiles **6** - **22** (pseudo first-order conditions), the absorbance of the vinyl cation was generally observed to undergo mono-exponential decay, as shown for the reaction of **2** with **9** (Scheme 3) in Figure 3a.[51] Least-squares fitting of the single-exponential function $A_t = A_0 e^{-k_{obs}t} + C$ (A_0 and A_t are the absorbances at time 0 and time t, respectively, and C is a constant) to the absorbance decay curve for the reaction of **2** or **3** with a nucleophile yielded k_{obs} (s^{-1})for the particular concentration of nucleophile.

Scheme 3. Generation of vinyl cation **2** by laser flash photolysis of **4-Br** in MeCN, and subsequent reaction with pyrrole **9**.



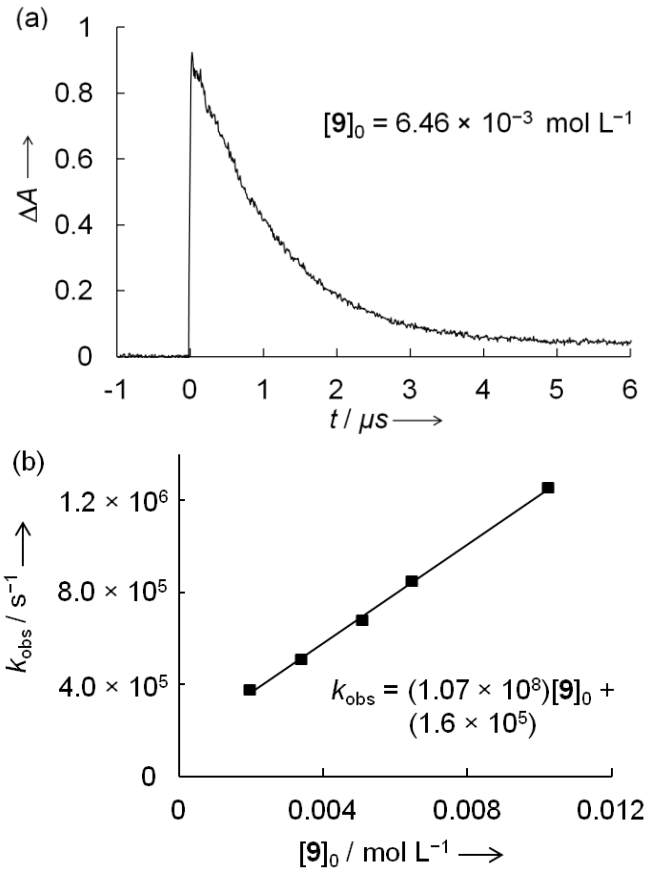


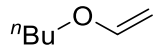
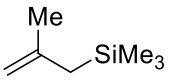
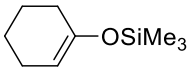
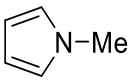
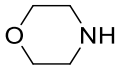
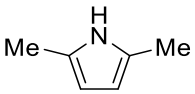
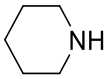
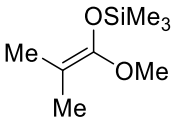
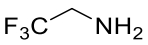
Figure 3. (a) Decay curve (λ = 350 nm) for the reaction of vinyl cation **2** with pyrrole **9**; (b) The second order rate constant *k* was obtained from the slope of the plot of k_{obs} vs. [**9**]$_0$.

Plots of the pseudo-first-order rate constants k_{obs} vs concentrations of the nucleophile were linear (see Figure 3b) and can be expressed by equation 3:

$$k_{obs} = k[\mathrm{Nu}] + k_{solv} \qquad (3)$$

where [Nu] is the molar concentration of the nucleophile, *k* (the slope of a plot of k_{obs} vs. [Nu]) is the second-order rate constant for the reaction of vinyl cation with nucleophile (values in Table 3), and the intercept is the first-order rate constant for the reaction of the vinyl cation with solvent (k_{solv}). Nine of the 14 correlations in acetonitrile showed intercepts in the range $(1.4 – 1.7) \times 10^5$ s^{-1}, which we ascribe to the reaction of **2** with acetonitrile. The only strong deviation from this value (6×10^6 s^{-1}, for the reaction of **2** with the strong nucleophile **20**) is likely to be a consequence of the problematic extrapolation of the very large rate constants to the concentration [**20**] = 0. Whereas the intercept for the correlation of k_{obs} vs. [Bu$_4$N]Cl (**13**) in trifluoroethanol agrees exactly with the previously reported rate constant for the reaction of **2** with trifluoroethanol (nucleophile **23**), for unknown reasons the corresponding plot of k_{obs} vs. [Bu$_4$N]Br (**14**) gives an intercept which is two times larger.

Table 3. Second-order rate constants, k (20 °C), for the reactions of vinyl cation **2** with nucleophiles **6-22** (solvent MeCN unless otherwise indicated).

Nucleophile		k (L mol^{-1} s^{-1})	Nucleophile		k (L mol^{-1} s^{-1})
	**6**	1.64×10^5	^{t}BuNH$_2$	**15**	1.23×10^7
	**7**	3.10×10^5	^{i}PrNH$_2$	**16**	4.64×10^7
	**8**	1.30×10^6	Et$_2$NH	**17**	1.28×10^8
	**9**	1.07×10^8		**18**	2.18×10^8
	**10**	3.17×10^8		**19**	6.88×10^8
	**11**	1.50×10^7	^{n}Bu$_4$N$^+$OAc$^-$	**20**	4.79×10^9
	**12**	6.01×10^6	^{n}Bu$_4$N$^+$OMs$^-$	**21**	5.99×10^7
^{n}Bu$_4$N$^+$Cl$^-$	**13**	8.06×10^5 [a]	^{n}Bu$_4$N$^+$I$^-$	**22**	*ca.* 4.4×10^9 [b]
^{n}Bu$_4$N$^+$Br$^-$	**14**	3.67×10^6 [a]			

[a] Solvent = 2,2,2-trifluoroethanol (TFE).

[b] Approximate rate constant derived from an experiment with a single concentration of [Bu$_4$N]I. See details in Supporting Information, p S25.

Monoexponential decays of the absorbances of the vinyl cations **2** and **3** were also observed when they were generated in trifluoroethanol (**23**) and in the solvent mixtures **24-41** (see Figure 4 for an example), and the first-order rate constants k_{obs} were obtained from fitting of $A_t = A_0e^{-k_{obs}t} + C$ to the decay curves. However, k_{obs} did not increase linearly with [H$_2$O] (Figure 5) and remained almost constant when the water content was raised beyond 20% v/v H$_2$O, in line with previous reports on the consumption of benzhydrylium[38,52] and tritylium ions[52] in MeCN/H$_2$O mixtures. Since a similar situation was also observed for other solvent mixtures, Table 4 lists the first-order rate constants $k = k_{obs}$ for reactions of **2** with the solvent nucleophiles **23-41**.

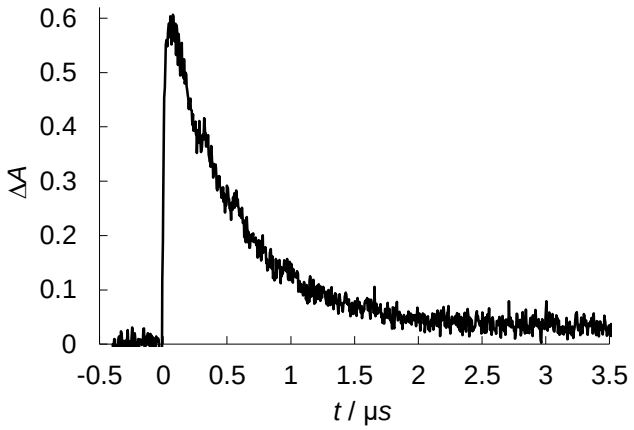


Figure 4. Decay curve (λ = 350 nm) from the reaction of vinyl cation **2** with 67:33 MeCN/EtOH (**32**).

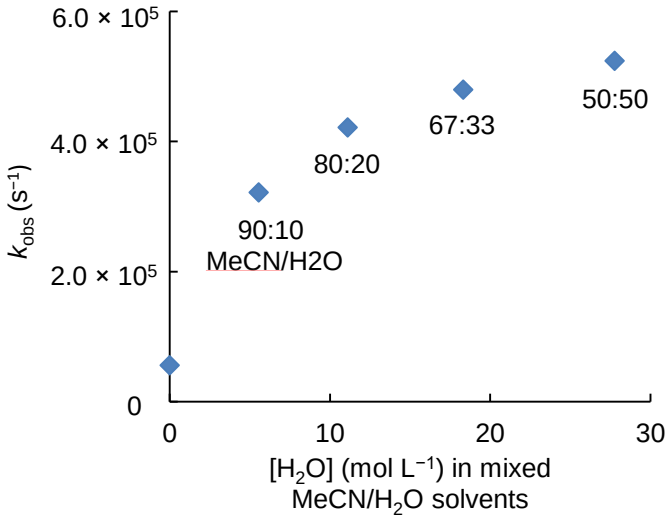


Figure 5. Plot of k_{obs} for the consumption of **2** in MeCN/H_2O solvents vs. concentration of H_2O.

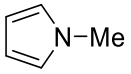
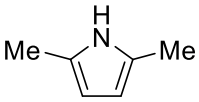
Table 4. Observed first-order rate constants, k (20 °C), for the reactions of vinyl cation **2** with solvent nucleophiles **23-41**.

Nucleophile		k (s^{-1})
TFE	**23**	1.4×10^{4} [a]
TFE/H_2O (90:10)	**24**	2.47×10^{4}
TFE/H_2O (60:40)	**25**	6.86×10^{4}
MeCN/H_2O (90:10)	**26**	3.22×10^{5}
MeCN/H_2O (80:20)	**27**	4.22×10^{5}
MeCN/H_2O (67:33)	**28**	4.80×10^{5}
MeCN/H_2O (50:50)	**29**	5.24×10^{5}
MeCN/EtOH (90:10)	**30**	6.06×10^{5}
MeCN/EtOH (80:20)	**31**	1.05×10^{6}
MeCN/EtOH (67:33)	**32**	2.01×10^{6}
MeCN/EtOH (50:50)	**33**	3.02×10^{6}
MeCN/EtOH (33:67)	**34**	4.13×10^{6}
MeCN/EtOH (20:80)	**35**	5.14×10^{6}
MeCN/EtOH (10:90)	**36**	6.93×10^{6}
EtOH/H_2O (40:60)	**37**	1.47×10^{6}
EtOH/H_2O (50:50)	**38**	1.61×10^{6}
EtOH/H_2O (60:40)	**39**	1.77×10^{6}
EtOH/H_2O (80:20)	**40**	2.88×10^{6}
EtOH/H_2O (90:10)	**41**	4.03×10^{6}

[a] Rate constant taken from ref 33.

Second-order rate constants for the reactions of **3** with pyrroles **9** and **10** and first-order rate constants for the reactions of **3** with the solvents **23**-**27**, **30**, and **31** were derived in a similar manner to that described above for vinyl cation **2**. The rate constants determined in this way are shown in Table 5.

Table 5. Rate constants, k (20 °C), for the reactions of vinyl cation **3** with π-nucleophiles **9** and **10** and with solvent nucleophiles **23-27**, **30**, and **31**.

Nucleophile		k
	**9**	3.19×10^8 L mol^{-1} s^{-1} [a]
	**10**	1.21×10^9 L mol^{-1} s^{-1} [a]
TFE	**23**	2.3×10^5 s^{-1} [b]
TFE/H_2O (90:10)	**24**	5.85×10^5 s^{-1}
TFE/H_2O (60:40)	**25**	1.76×10^6 s^{-1}
MeCN/H_2O (90:10)	**26**	1.30×10^7 s^{-1}
MeCN/H_2O (80:20)	**27**	1.46×10^7 s^{-1}
MeCN/EtOH (90:10)	**30**	1.62×10^7 s^{-1}
MeCN/EtOH (80:20)	**31**	2.70×10^7 s^{-1}

[a] Solvent = MeCN

[b] Rate constant taken from ref 33. TFE = 2,2,2-trifluoroethanol.

Correlations and Discussion

In numerous investigations we have shown that the second-order rate constants k for the reactions of electrophiles with nucleophiles at 20 °C may be calculated using equation 4,

$$\lg k\ (20\ °C) = s_N\,(E + N) \qquad (4)$$

where E characterizes the electrophilicity of the electrophile (treated as being solvent-independent), while N represents the nucleophilicity of the nucleophile, and s_N is a nucleophile-specific susceptibility parameter.[24,53] Whereas new N and s_N parameters of nucleophiles are derived from linear plots of lg k vs. the known E parameters of the reference electrophiles, new E parameters of electrophiles have been derived from linear correlations between (lg k)/s_N and N of the reference nucleophiles.

Following this procedure, (lg k)/s_N was plotted vs. N for all investigated nucleophiles with known nucleophilicity parameters (Figure 6). As the published reactivity parameters N and s_N

for nucleophiles **6** – **20** refer to second-order rate constants in acetonitrile, while those for solvents **23** – **41** (designated N_1) refer to first-order rate constants, it is possible to plot the logarithms of the second-order rate constants for the π-systems **6** – **11**, the amines **12** and **15** – **19**, and the anions **13**, **14**, **20** as well as those of the first-order rate constants for the solvents **23** – **41** side by side in Figure 6. The remarkably good correlation for these diverse nucleophiles over a reactivity range of more than 16 orders of magnitude shows that the nucleophilic reactivities toward vinyl cation **2** (*sp*-electrophile) follow the same pattern as those toward benzhydrylium ions. However, equation (4) is not fulfilled because the slope of this correlation is 0.53 and not 1.0, as required by equation (4), showing that **2** is substantially less sensitive to changes in the reactivity of the nucleophile than benzhydrylium ions (sp^2-electrophiles).

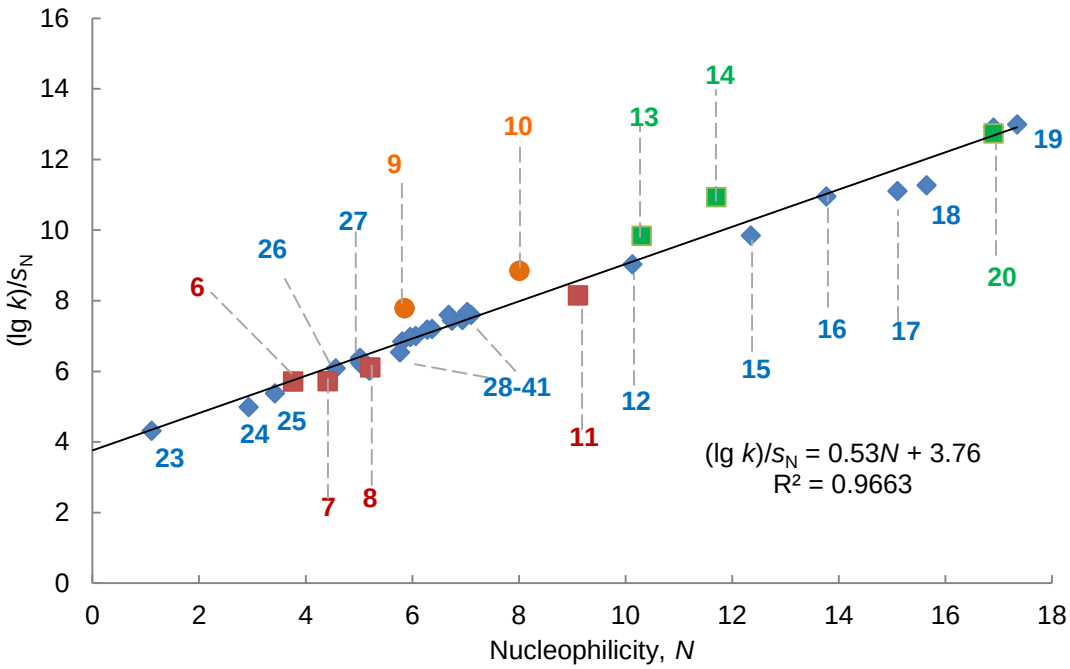


Figure 6. Plot of (lg k/s_N) vs. N for the reactions of vinyl cation **2** with nucleophiles **6-20** and **23-41**.

A similar plot, shown in Figure 7, was constructed using the first- and second-order rate constants k (listed in Table 5) for the reactions of vinyl cation **3** with a variety of nucleophiles. Again, a strong linear correlation is observed over a wide range of reactivity, and again a slope of much less than 1 is obtained. It is remarkable that even pyrrole **10** fits this correlation though the rate constant of 1.21×10^9 L mol^{-1} s^{-1} is already close to the diffusion control limit. Vinyl cation **3** thus shows very similar behavior to **2**. Its higher electrophilic reactivity may be due to reduced steric shielding of the cationic carbon center.

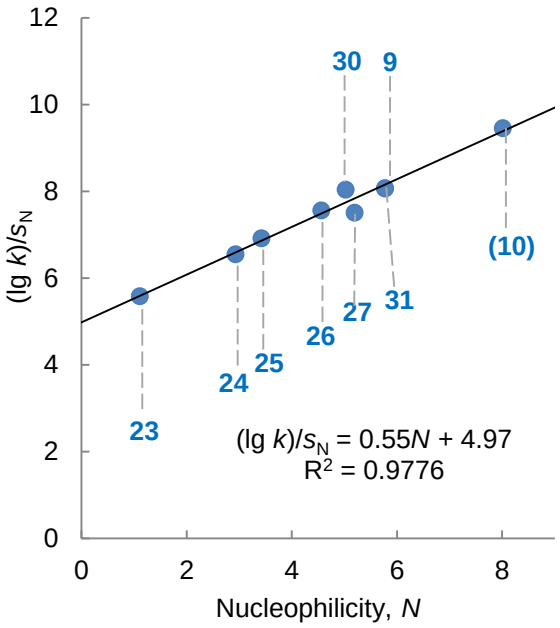


Figure 7. Plot of (lg k/s_N) vs. N for vinyl cation **3**, from its reactions with various nucleophiles.

Analogous linear correlations of (lg k/s_N) vs. N with slopes much smaller than 1 were previously found for S_N2 reactions of alkyl halides,[54] indicating that variation of the nucleophiles also had a smaller influence on the rate constants of the S_N2 reactions than on those for the reactions with benzhydrylium ions. Although the correlations shown in Figures 6 and 7 might also be mathematically expressed by adding an additional electrophile-specific susceptibility parameter s_E to eq. (4),[54] we refrain from deriving electrophilicity parameters E from the extended correlations. The reason is that E determined in this way would represent an approximate reactivity ranking toward very weak nucleophiles which react with rate constants close to 1 (lg k = 0), i. e., reactions which have little relevance in practice, because commonly used solvents react much faster.

For that reason, let us directly compare rate constants for the reactions of nucleophiles with vinyl cations **2** and **3** and with benzhydrylium ions **47** – **49** (Chart 2).

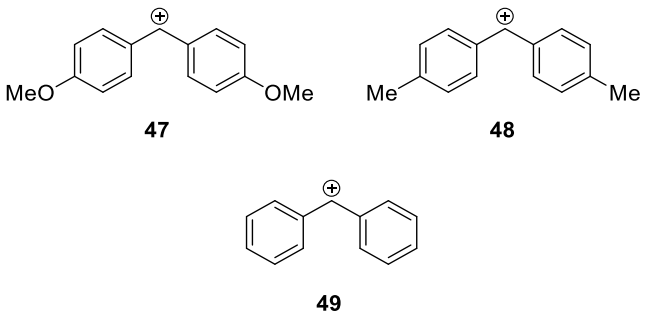


Chart 2. Benzhydrylium ions **47** - **49**.

In Figure 8, the lg *k* values for the reactions of **2** (values of *k* taken from Tables 3 and 4) are plotted against the corresponding lg *k* values for the reactions of benzhydrylium ion **47** (*k*(**47**) from Table S1 on p. 43-44 of the Supporting Information).[55] The plot shows a fair correlation between the two data sets and (similar to Figure 6) that the rate constants for the reactions with the vinyl cation **2** are less affected by variation of the nucleophiles than the corresponding rate constants for **47** (slope = 0.48). If we neglect the two pyrroles (**9** and **10**), which deviate significantly from the correlation, one can see that the vinyl cation **2** reacts faster than the dimethoxybenzhydrylium ion **47** with weak nucleophiles ($k < 5 \times 10^6$ s^{-1} or L mol^{-1}s^{-1}), while stronger nucleophiles react faster with benzhydrylium ion **47**. Overall, however, the vinyl cation **2** and the dimethoxybenzhydrylium ion **47** have comparable electrophilic reactivities.

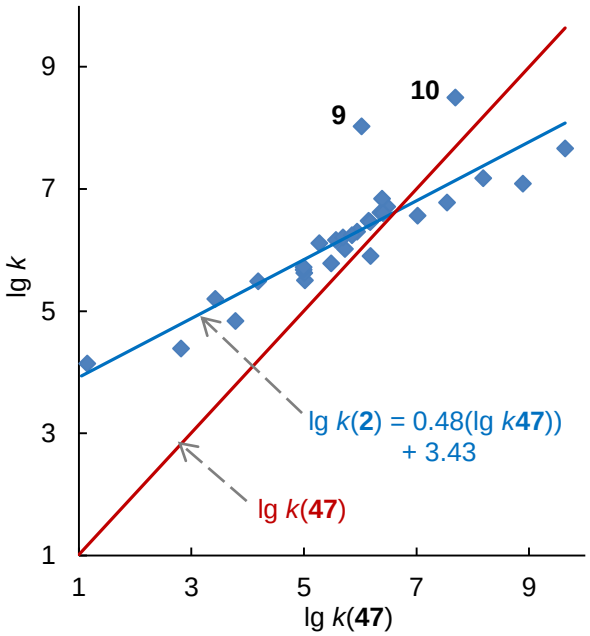


Figure 8. Correlation of lg *k* for the reactions of vinyl cation **2** with various nucleophiles (**6**-**16**, **23**-**41**) with lg *k* for the analogous reactions of the 4,4'-dimethoxybenzhydrylium ion **47**(from Table S1 in SI). The red line is a plot of lg *k*(**47**) against itself to highlight the crossing range where nucleophiles react with equal rates with **2** and **47**.

An analogous comparison can be made between vinyl cation **3** and benzhydrylium ion **48**. A plot of lg *k* for the reactions of **3** with various nucleophiles vs. lg *k* for the corresponding reactions of **48** (*k*(**48**) from Table S2 on p. S44 of the Supporting Information) shows a good linear correlation (Figure 9),[56] with a slope significantly less than 1 (slope = 0.56). Vinyl cation **3** thus has an electrophilicity comparable to that of **48**.

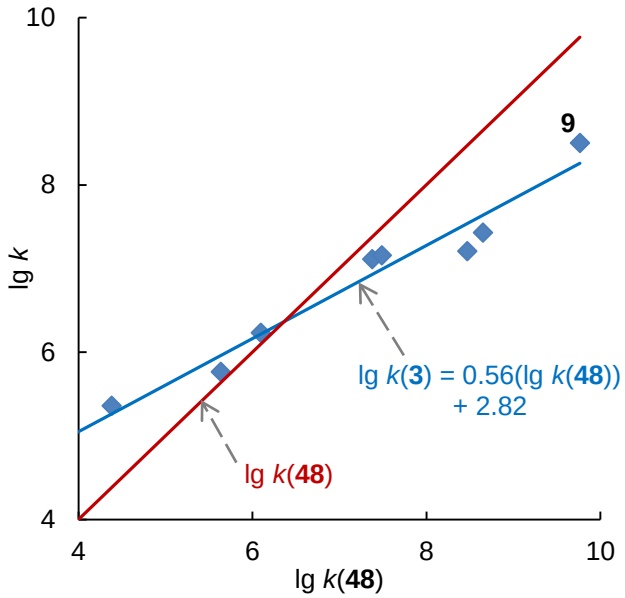


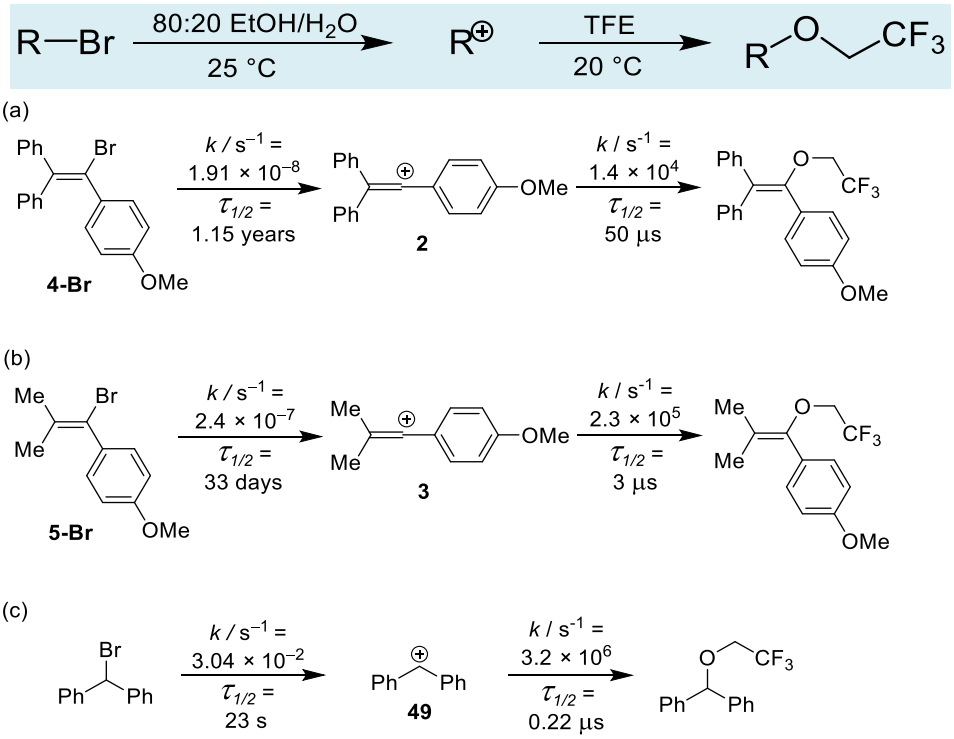
Figure 9. Correlation of lg *k* for the reactions of vinyl cation **3** with various nucleophiles (**9**, **23**-**27**, **30**, **31**) with lg *k* for the analogous reactions of the 4,4'-dimethylbenzhydrylium ion **48** (from Table S2 in SI). The red line is a plot of lg *k*(**48**) against itself to highlight the crossing range where nucleophiles react with equal rates with **3** and **48**.

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The observation that vinyl cations **2** and **3** show reactivities toward nucleophiles that are similar to the corresponding reactivities of the donor-stabilized benzhydrylium ions **47** and **48** appears surprising at first glance, as the latter species are formed much faster in S_N1 reactions than the corresponding vinyl derivatives. In fact, the ionizations of the benzhydryl bromides, which yield the highly stabilized benzhydryl cations **47** and **48,** are so fast in aqueous ethanol that it is not possible at present to measure their solvolysis rates.

Therefore, we compare here the solvolyses of the vinyl bromides **4-Br** and **5-Br** with that of Ph_2CHBr (for which experimental data are available). Scheme 4 shows that the benzhydryl bromide solvolyzes 10^5 to 10^6 times faster in 80% aqueous ethanol at 25 °C than the vinyl bromides **4-Br** and **5-Br**. Despite its much faster rate of formation, the parent benzhydrylium ion reacts one to two orders of magnitude faster with trifluoroethanol at 20 °C than **2** or **3** (compare the second reactions in each of Scheme 4a, 4b and 4c). Similar rate ratios have been found for activation-controlled reactions of these electrophiles with numerous other nucleophiles (i. e. reactions which do not proceed with diffusion controlled rates).

Scheme 4. Solvolysis reactions of (a) **4-Br**,[a] (b) **5-Br**,[b] and (c) Ph_2CHBr [c] in 80:20 EtOH/H_2O at 25 °C, and reactions of cations **2**, **3**, and **49** with TFE at 20 °C.



[a] For the first step of reaction (a), a value of $k = 1.92 \times 10^{-4}$ s^{-1} was measured at 120 °C;[39d] reported activation parameters allow extrapolation to value at 25 °C given in the Scheme. The rate constant for the second step is taken from reference 33.

[b] For the first step of reaction (b), a value of $k = 8.78 \times 10^{-4}$ s^{-1} was measured at 120 °C;[40c] reported activation parameters allow extrapolation to value at 25 °C given in the Scheme. The rate constant for the second step is taken from reference 33.

[c] The rate constant for the first step of (c) is from reference 57. The rate constant for the second step is from reference 58.

Laser flash experiments have shown that the reactions of the parent benzhydrylium ion **49** with Br^- are diffusion-controlled in all alcoholic solvents investigated.[19] As there is no barrier for the ion combination, the principle of microscopic reversibility implies that the transition state for the heterolytic cleavage of Ph_2CHBr corresponds to the ion-pair, as illustrated in Figure 10.

In contrast, the reaction of Br^- with vinyl cation **2** is activation controlled, proceeding with a rate constant of 3.7×10^6 L mol^{-1} s^{-1} in TFE (Table 3). For the same reaction in 80 % aqueous ethanol one can calculate $k = 7.4 \times 10^6$ L mol^{-1} s^{-1} from $N = 14.5$, $s_N = 0.6$ (for Br^- in 80 % aqueous ethanol)[19] using the correlation equation given in Figure 6. As this reaction is not diffusion controlled, transition state theory can be applied to calculate an activation energy of $\Delta G^{\ddagger} = 8.1$ kcal mol^{-1} for the ion combination in 80 % aqueous ethanol (Figure 10, right hand side). The kinetic data implies that the heterolyses of Ph_2CHBr and **4-Br** have almost identical $\Delta G°$ values, as shown in Figure 10.

Figure 10 clearly illustrates that the major reason for the different solvolysis rates of Ph_2CHBr and **4-Br** is the difference in the intrinsic barriers (since the Gibbs energies of reaction $\Delta G°$ are very similar). Hence, the transition state of the first step of the S_N1 reaction of **4-Br** cannot be carbocation-like i.e. it does not correspond to the ion pair of Br^- with vinyl cation **2**. We demonstrate explicitly below using quantum chemical calculations that $\Delta\Delta G° = \Delta G°_{Ph_2CHBr} - \Delta G°_{\mathbf{4\text{-}Br}}$ is indeed negligible (*vide infra*), as derived from kinetic data for the construction of Figure 10.

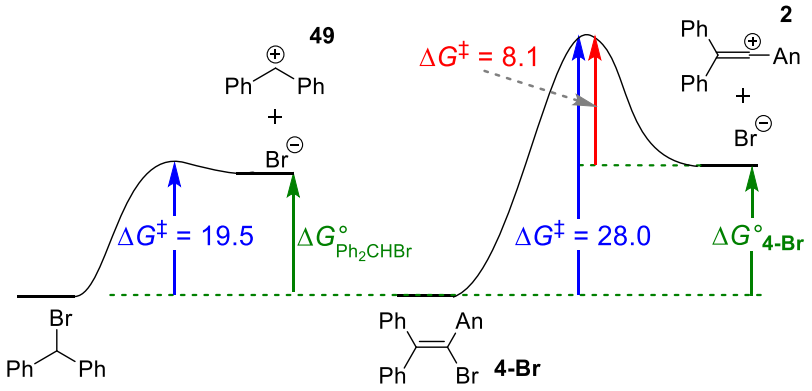


Figure 10. Schematic Gibbs energy profiles (kcal mol^{-1}) for the ionization of benzhydryl bromide and vinyl bromide **4-Br** in 80% aqueous ethanol at 25 °C. $\Delta G^‡$ values were calculated using the Eyring equation (for the solvolysis reactions, rate constants from Scheme 4a and 4c were used; see main text for details of the calculation for addition of Br^- to **2**).

Common Ion Rate Depression

Although S_N1 reactions are usually accelerated when the polarity of the solvent is increased by salt additives,[1c,d,h,59] in certain cases, the opposite effect is observed. Common ion rate depression is a phenomenon whereby the rate of a solvolysis reaction k_{obs} is slowed by addition of a salt containing the anion of the leaving group (X^-).[1h,19,27,60] It is observed when the recombination of the carbocation R^+ with X^- is faster than addition of the solvent to R^+ (with first order rate constant k_{solv}); i.e., when $k_{-1}[X^-] \geq k_{solv}$ (see Scheme 5, and equation (5), in which the full expression for k_{obs} is given, and $\alpha = k_{-1}/k_{solv}$).

Scheme 5. Reversible heterolysis of RX to give R^+, which may react with solvent (completing the solvolysis) or revert to RX by reaction with X^-.

$$R{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^{\ominus} + R^{\oplus} \xrightarrow[k_{solv}]{SolvOH} R{-}O{-}Solv + HX$$

$$k_{obs} = \frac{k_1 k_{solv}}{k_{solv} + k_{-1}[X^-]} = \frac{k_1}{1 + \alpha[X^-]} \qquad (5)$$

As highly reactive carbocations are immediately trapped by the solvent, which is present in high concentration, common ion return is only observed when highly stabilized carbocations are generated in solvents of low nucleophilicity. Since vinyl cations had been considered to be highly reactive because of their slow formation in S_N1 processes, the observation of common ion rate depression in S_N1 processes was highly surprising, and the numerous attempts to rationalize this phenomenon have been summarized.[60b] With the knowledge that vinyl cations **2** and **3** have relatively low electrophilic reactivities, similar to those of the highly stabilized benzhydrylium ions **47** and **48** (see Figures 8 and 9), two systems for which common ion depression has generally been observed,[19] it is no longer surprising that this effect was also found for the solvolyses of **4-X** and **5-X** (X = Cl, Br).[60b]

In previous work we have demonstrated that the occurrence of common ion rate depression can be derived from the directly measured rate constants of the reactions of the independently generated carbocations with the anionic leaving groups (i. e. X^-) and the solvent.[19] From the rate constants in Tables 3 and 4 for the reactions of **2** with Cl^- in TFE (8.06×10^5 L mol^{-1} s^{-1}), Br^- in TFE (3.67×10^6 L mol^{-1} s^{-1}), and TFE (1.40×10^4 s^{-1}), respectively, one can calculate α values of 58 and 262, respectively, in good agreement with common ion rate depressions observed for similar systems under comparable conditions.[61]

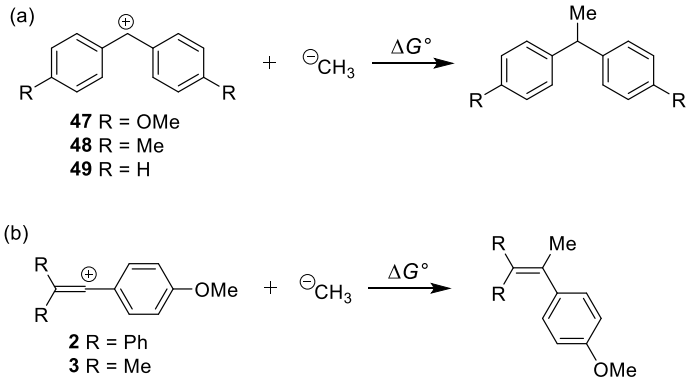
Computational Analysis

Directly measured rate constants as well as the observation of common ion rate depression thus indicate that vinyl cations are sluggish electrophiles, despite their very slow formation in S_N1 reactions. By combining the experimentally determined rate constants for the solvolysis reactions and ion recombinations (see Figure 10 and associated discussion above), we had derived that $\Delta G°$ for the heterolytic cleavage of the C-Br bond in Ph_2CHBr is almost the same as that for heterolysis of **4-Br**. This conclusion is in line with quantum chemical calculations, as we show below.

Recently, we have calculated[62] gas phase methyl anion affinities of benzhydrylium ions as a measure for their relative Lewis acidities (Scheme 6, table entries 1 – 3).[12] Comparison with entries 4 and 5 shows that the methyl anion affinities of vinyl cations **2** and **3** are closely similar to that of the unsubstituted benzhydrylium ion (**49**), as derived from the rate constants for forward and backward reactions in Figure 10.[63] Kinetic data and quantum chemically calculated Lewis acidities thus agree on the conclusion that the differences in intrinsic barriers account for the fact that vinyl cations **2** and **3**, despite their much higher Lewis acidities, are

not more electrophilic than the highly stabilized benzhydrylium ions **47** and **48**, respectively (Figures 8 – 9 and associated discussion).

Scheme 6. Calculated Gibbs energies of reactions[a] of methyl anion with benzhydrylium ions **47**-**49** and of vinyl cations **2** and **3** (methyl anion affinities) in the gas phase.



Entry		R	$\Delta G°$ (kcal mol^{-1})
1	**47**	OMe	–178.9 [b]
2	**48**	Me	–188.6 [b]
3	**49**	H	–197.7 [b]
4	**2**	Ph	–198.2 [c]
5	**3**	Me	–200.2 [c]

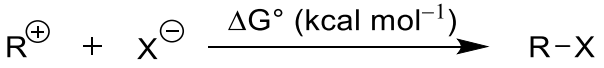
[a] Computational method and basis set employed for all values of $\Delta G°$: B3-LYP/6-311++G(3df,pd)//B3LYP/6-31G(d,p).[62,64]

[b] Calculated value reported in reference 12.

[c] This work.[62,63,64]

The calculations shown in Table 6 confirm that in the gas phase, Ph_2CH^+ and **2** also have almost equal affinities toward Br^- ($\Delta\Delta G°$ = 0.9 kcal mol^{-1}, entries 1, 2) and Br^- solvated by one molecule of water ($\Delta\Delta G°$ = 1.1 kcal mol^{-1}, entries 3, 4), in agreement with our observations based on the kinetic data (Figure 10, above). As expected, the ion combinations are calculated to be much less exergonic in solution (entries 5 – 8), but the very small calculated values of $\Delta G°$ in aqueous solution indicate that the PCM model significantly overestimates the ion solvation energies. [65]

Table 6. Calculated Gibbs energies of the reactions[a] of Br^- (and Br^- solvated by 1 water molecule) with the parent benzhydrylium ion (**49**) and vinyl cation **2** in the gas phase and in aqueous solution.[b]



Entry	R^+	X^-	Gas Phase / Solvent Model	$\Delta G°$ (kcal mol^{-1})
1	Ph_2CH^+	$Br^⊖$	Gas	−113.9
2	**2**	$Br^⊖$	Gas	−114.8
3	Ph_2CH^+	$Br^⊖(H_2O)_1$	Gas	−102.1
4	**2**	$Br^⊖(H_2O)_1$	Gas	−103.2
5	Ph_2CH^+	$Br^⊖$	Water	−9.5
6	**2**	$Br^⊖$	Water	−15.3
7	Ph_2CH^+	$Br^⊖(H_2O)_1$	Water	−5.8
8	**2**	$Br^⊖(H_2O)_1$	Water	−11.6

[a] Computational method and basis set employed for all values of $\Delta G°$: TPSS/def2TZVP+GD3.[66,67]

[b] PCM; method TPSS/def2TZVP+GD3. See Table S7 (p S83 of Supporting Information) for further quantities determined from these calculations.

When trying to localize the transition states for the heterolytic cleavage reactions of **4-Br** and Ph_2CHBr in aqueous solution (i.e., the reactions in Figure 10) by the DFT method TPSS/def2TZVP+GD3 using the PCM continuum solvent model,[68] we observed a continuous increase of the potential energy (E_{tot}) as the C-Br bond length was elongated, and the ion pair was reached without passing through a maximum in E_{tot} (Figure 11). The same result was found when one molecule of water was explicitly considered (see Figure S4 in SI, p S84). In both cases, the gradient was much larger for the vinyl bromide due to the higher force constant of the C_{sp^2}-Br bond.

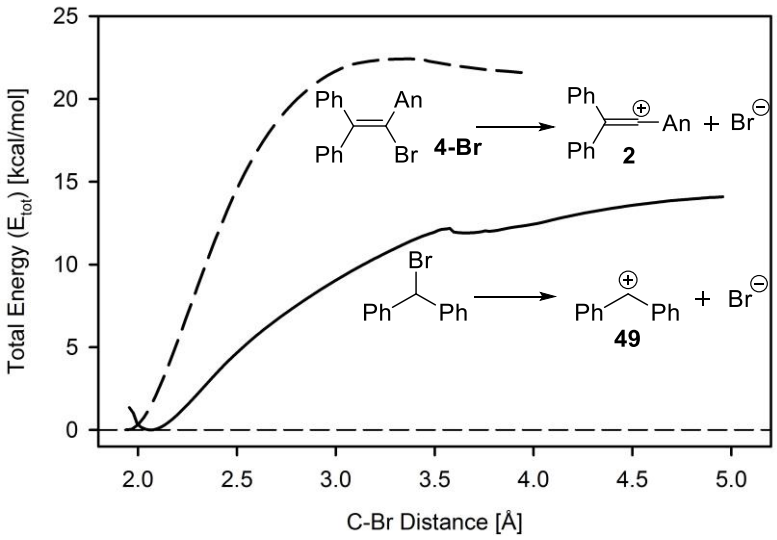
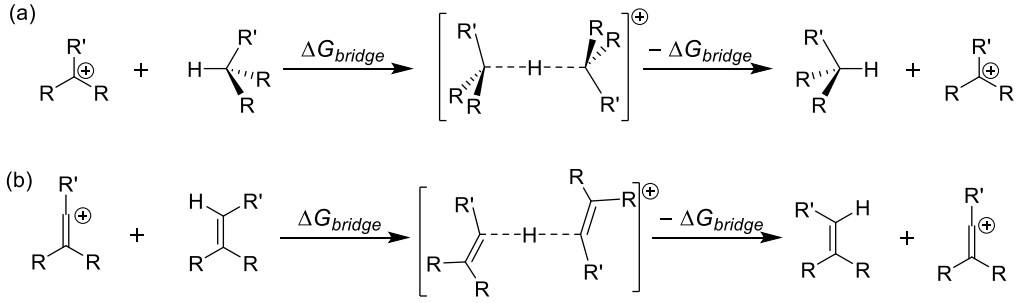


Figure 11. Intrinsic reaction coordinate calculations for the cleavage of the C-Br bond in **4-Br** and Ph_2CHBr (Total energies E_{tot}; TPSS/def2TZVP+GD3; PCM (solvent = water)).

The fact that the maximum of total energy in the **4-Br** graph of Figure 7 is slightly lower than ΔE_{tot} calculated for the reaction of **2** with Br^- in water (−24.9 kcal mol^{-1}, see Table S7 in SI on p S83) may be due to the PCM-model used for the calculations on the heterolysis reactions and on the separated species and to the fact that for longer C-Br distances the closed-shell restriction does not apply. A computational assessment of the transition state for the vinyl bromide heterolysis (for which the activation barrier was unequivocally deduced from kinetic data – see Figure 10 and associated discussion) might be possible by explicit consideration of more solvent molecules. However, general problems of this type of treatment have recently been pointed out by Singleton,[69] and in any case, this approach is beyond the scope of this investigation.

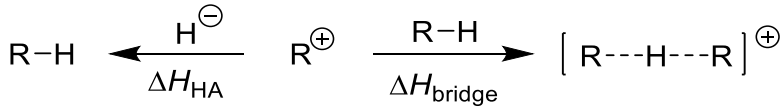
As mentioned in the Introduction, the intrinsic barrier in the Marcus equation ($\Delta G_0^{\ddagger}$) corresponds to the Gibbs activation energy of an identity reaction. Since there are no identity reactions for the ion combinations in eq. (1), we analyzed the intrinsic barriers for the identity hydride transfers illustrated in Scheme 7 as models for the transition states of $sp^3 \rightleftharpoons sp^2$ and $sp^2 \rightleftharpoons sp$ rehybridizations (Table 7).[70]

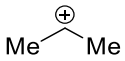
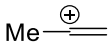
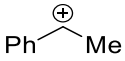
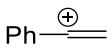
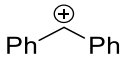
Scheme 7. Formation of (a) tricoordinated and (b) dicoordinated hydrido-bridged carbenium ions [R---H---R]$^+$ from the isolated carbenium ion R$^+$ and its parent compound, RH (without considering species showing aromatic interactions (π-stacking)).



The left part of Table 7 allows comparison of quantum chemically calculated and experimental gas-phase hydride affinities for several tri- and di-coordinated carbenium ions.[71] While the absolute hydride affinities calculated with different basis sets differ considerably (see Supporting Information, p. S69-70), there is good agreement between relative hydride affinities obtained with different computational methods and experimental data.

Table 7. Comparison of Calculated and Experimental Gas Phase Values ΔH_{HA} (298 K) and ΔG_{HA} (298 K) for Additions of H^- to Various Carbenium Ions (Hydride Affinity = $-\Delta H_{HA}$), and Calculated Intrinsic Barriers ΔH_{bridge} and ΔG_{bridge} for the Hydride Transfer Reactions:



Entry	R^+	Experimental ΔH_{HA} [a]	Calculated Quantities [b]			
			ΔH_{HA} [b]	ΔG_{HA} [b]	ΔH_{bridge} [b]	ΔG_{bridge} [b]
1		−251.8	−259.3	−251.8	−18.5	−8.1
2		−264.9	−272.4	−264.2	−14.9	−2.9
3		−225.1	−234.5	−228.0	−12.2	+0.3
4		−239.7	−247.5	−240.1	−3.8	+8.2
5		−239.3	−246.8	−240.6	−12.9	−1.9
6		-	−220.9	−212.8	−8.0	+3.3

[a] Experimental data (kcal mol^{-1}) listed in ref 30.

[b] Calculated values from this work. Method and basis set employed: TPSSTPSS/def2TZVP+GD3//TPSSTPSS/def2TZVP+GD3. Units are kcal mol^{-1}.

Table 7 shows, for example, that successive replacement of the methyl groups in the isopropyl cation by phenyl (i.e., giving first phenethyl cation and then benzhydryl cation) reduces the hydride affinities by 25 and then 15 kcal mol^{-1} in calculated ΔH_{HA} and ΔG_{HA} (entries 1, 3, 6) and in experimentally determined ΔH_{HA}. The hydride affinities of the vinyl cations (entries 2 and 4) are 13 kcal mol^{-1} larger than those of the corresponding saturated analogues (entries 1 and 3).

Hydride transfer to tri- or di-coordinated carbenium ions from their parent alkanes or alkenes occurs through hydrido-bridged species (Scheme 7). The enthalpies and Gibbs energies (ΔH_{bridge} and ΔG_{bridge}, respectively) of formation of these entities from the isolated reactants, i. e., the intrinsic barriers for the hydride transfers are shown in the right hand columns of Table 7. Whereas the hydrido-bridged species from isopropyl cation/propane (entry 1) and benzyl cation/toluene (entry 5) are minima on the potential energy surface (gas phase), all other hydrido-bridged species correspond to transition states (Table 7, and Tables S4-S6 in Supporting Information p. S71-S75). All minima and all transition states have a negative ΔH_{bridge} with respect to the isolated reactants. As expected, the tendency to undergo hydrido-bridging decreases with decreasing hydride ion affinity, i.e., for tricoordinated carbenium ions, ΔG_{bridge} increases in the order $1 < 5 \approx 3 < 6$ and in the order entry 2 < entry 4 for dicoordinated carbenium ions.

In the context of our analysis, the comparisons of entries 2 and 1 and of entries 4 and 3 are of particular importance. Although the vinyl cations in entries 2 and 4 have significantly higher hydride affinities compared to their saturated analogs in entries 1 and 3, respectively, their hydrido-bridging tendencies are much smaller. As the hydrido-bridged complexes represent models for the transition states of $sp^3 \rightleftharpoons sp^2$ and $sp^2 \rightleftharpoons sp$ rehybridizations (Scheme 7), the 8 kcal/mol lower tendency towards hydrido-bridging of the phenyl-substituted vinyl cation in entry 4 compared to the saturated analog in entry 3 reflects the high intrinsic barriers which are responsible for the low rates of vinyl halide heterolyses (low electrofugalities[15] of vinyl cations) and the low rates of nucleophilic addition to vinyl cations (low electrophilicities[15] of vinyl cations).

Conclusion

Discussions of carbocation reactivities are generally based on the assumption that the transition states of S_N1 reactions are carbocation-like (Hammond postulate), and that the slower a carbocation is formed in an S_N1 process, the faster it will react with a nucleophile. Although deviations from this rule have previously been reported, including literature reports on

comparatively low absolute rate constants for reactions of vinyl cations with nucleophiles and common ion rate depression in solvolyses of vinyl derivatives (typical for carbocations of relatively low reactivity), the consequences of these observations for the interpretation of vinyl cation chemistry have rarely been considered.

We have now shown that the transition states of vinyl halide solvolyses are often not carbocation-like. Consequently, the influence of intrinsic barriers on this step cannot be neglected. The approximation to consider only the thermodynamic term (i. e., ΔG^0 of the ionization step) for analyzing the kinetic behaviour of carbocations, which works well for the reactions of most weakly stabilized tricoordinated carbenium ions, cannot be applied for vinyl cations. Vinyl cations (i.e., dicoordinated carbenium ions) are weaker electrofuges as well as weaker electrophiles than tricoordinated carbenium ions of similar Lewis acidity because of the high intrinsic barriers for $sp^2 \rightleftharpoons sp$ rehybridizations.

Supporting Information

Experimental procedures and characterization of representative products; details of kinetic experiments with vinyl cations **2** and **3**; literature rate constants used for the construction of Figures 8 and 9; copies of NMR spectra; details of quantum chemical calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI:_

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