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Production of α-Siloxycarbenium Ions by Protonation of Photochemically Generated α-Siloxycarbenes. Formation Mechanism and Reactivities with Nucleophiles

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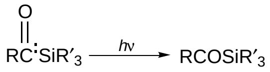
Abstract: The acyltrimethylsilanes 4-$RC_6H_4C(O)SiMe_3$ (R = H, Me, MeO) and β-naphthyl$C(O)SiMe_3$, upon photolysis in acetonitrile with 20 ns pulses of 248 nm light from an KrF* excimer laser, give rise to the corresponding α-siloxycarbenes $\mathrm{Ar\dot{C}OSiMe_3}$, whose absorption spectra (λ_{max} between 270 and 310 nm), lifetimes (between 130 and 260 ns), and reactivities with proton donors (ROH, mainly alcohols) are reported. With highly acidic ROH, such as 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP), the reaction is of simple second order, rate constants being in the 10^9 M^{-1} s^{-1} range and virtually independent of the nature of the aromatic moiety of the carbene. Isotopic substitution of H in ROH by D has no effect on the rate constant for reaction with carbene. For less acidic alcohols such as, e.g., methanol, the reactivity of the carbenes increases with increasing [ROH]. This behavior is interpreted in terms of reversible adduct formation between carbene and alcohol followed by reaction with further alcohol molecule(s) to give product. On the basis of experiments in the acidic and only weakly nucleophilic solvents 2,2,2-trifluorethanol (TFE) and HFIP, protonation of the carbenes leads to the corresponding carbenium ions, whose absorption spectra (λ_{max} between 305 and 355 nm), lifetimes (100 ns−5 μs in TFE), and reactivities with nucleophiles (halides, alcohols, and ethers) are reported. In the solvent HFIP, the reactivities of the carbenium ions with the alcohols and ethers increase with their concentration, in a way analogous to that observed in the reaction of the carbenes with the alcohols. This is explained as resulting from reversible formation of a cation−nucleophile complex followed by reaction of the complex with a second nucleophile molecule which acts as a base. In solvents more basic than HFIP, it is presumably the solvent which serves this function.

Introduction

The reaction of a series of diarylcarbenes with ROH has recently been shown to involve protonation (eq 1) yielding the corresponding carbenium ions (benzhydryl cations) which were identified using nanosecond optical and conductance detection methods.[3] Experiments with picosecond time resolution[4] are in support of the protonation mechanism suggested,[3,5−7] the lifetime of the parent diphenylcarbenium ion in neat aliphatic alcohols being in the 40−90 ps range.[4]

$$Ar_2C: + ROH \rightarrow Ar_2CH^+ + RO^- \qquad (1)$$

Benzhydryl cations are obviously highly stabilized, due to the delocalization of the positive charge over *two* aromatic rings, and thus the driving force for cation formation from the carbene should be considerable. With the less stabilized *benzyl* systems there is, in principle, the possibility that protonation of the carbene by O−H bonds to give the cation is thermodynamically unfavorable. We have, for this reason, studied a series of para-substituted phenylcarbenes and a naphthylcarbene carrying the trimethylsiloxy group. These carbenes can be conveniently generated from the corresponding acyltrimethylsilanes by photolysis (eq 2),[8,9]



$$\mathrm{R\overset{\overset{O}{\|}}{\dot{C}}SiR'_3 \xrightarrow{h\nu} RCOSiR'_3} \qquad (2)$$

and this method has recently been used to trap phenyltrimethylsiloxy carbene by reaction with pyridine yielding the corresponding ylide.[10] The formation of carbene has been shown[9] to proceed via the triplet state of the acylsilane. In the case of benzoyltrimethylsilane, the lifetime of the triplet in CH_2Cl_2 solution has been estimated to be 50−100 ns.[10] This sets a lower limit with respect to the lifetime of carbocations that may be produced by protonation of the carbenes generated from the acylsilane triplets. It has recently been shown[11−13] that lifetimes of highly reactive carbocations can be quite long in fluorinated alcohols (due to the solvents' low nucleophilicity), allowing their detection on the ≥nanosecond time scale. Due to the stabilizing

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effect of heteroatoms at the α-position, siloxy-substituted benzyl cations can be expected to have lifetimes in excess of that (20 ns) analyzable with the presently available apparatus. With respect to carbene protonation, fluorinated alcohols have the additional advantage of a high Brönsted acidity which is likely to lead to a high rate of conversion of carbene into carbenium ion, eq 3:

$$\mathrm{RC^{\cdot}OSiR'_3 + R''OH \rightarrow RCH^{+}OSiR'_3 + R''O^{-}} \qquad (3)$$

For these reasons, by studying the reactions of (photochemically produced) carbenes with and in acidic alcohols, it was hoped to gain new information relating not only to these carbenes and their nucleophilic reactivity but also to the carbenium ions derived from them by protonation. Since the carbenes are heteroatom (O) substituted at C_α, they can be expected to be singlet-state species. Mechanistic complications due to contribution of triplet reactions (from rapid singlet−triplet interconversion) can thus be regarded as unlikely.

Experimental Section

The solvents used were acetonitrile (AN; spectroscopic grade, from Merck), 2,2,2-trifluoroethanol (TFE; from Aldrich), or 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP; from Hoechst). TFE and HFIP were dried with Na_2SO_4 and then distilled over $NaHCO_3$ (to remove trace acid impurities). HFIP was additionally zone-refined to a purity ≥99.8%.

The benzoyltrimethylsilanes 4-$RC_6H_4C(O)SiMe_3$ (R = H, Me, MeO) and β-naphthyl$C(O)SiMe_3$ were synthesized as described[14] and chromatographed to a purity of ≥99% by preparative HPLC using a 30 cm Polygosil 60-10 NO_2 column (diameter 2.5 cm) and pentane:Et_2O 1:1 as eluent. The IR and NMR spectra were in agreement with those[14] reported in the literature. The aldehydes 4-RC_6H_4CHO could not be *completely* removed,[15] although their concentration could be kept below 0.5%. The purity was checked by GC on capillary columns (35 m OV17, 140 °C, and 24.5 m OV1, 150 °C). For product analysis experiments, deoxygenated 15 mM solutions of the silanes in methanol or 2,2,2-trifluoroethanol (TFE) with 0.01% pyridine added (to neutralize acid impurities) were photolyzed at 0 °C with the light of a high pressure Hg lamp (Hanau TQ 150) in a quartz reactor, and they were analyzed using GC, NMR, and HPLC techniques with authentic compounds for comparison. The mixed acetals $ArCH(OSiMe_3)OR$ were characterized by their ^1H NMR spectra ($CDCl_3$): Ar = Ph, R = Me: $\delta = 0.17$ (s, 9H), 3.2 (s, 3H), 5.8 (s, 1H), 7.1−7.7 (m, 5H); Ar = Ph, R = CH_2CF_3: $\delta = 0.1$, (s, 9H), 3.65 (qm, $J = 8.5$ Hz, 2H), 5.88 (s, 1H), 7.1−7.7 (m, 5H); Ar = 4-Me-C_6H_4, R = CH_2CF_3: $\delta = 0.17$ (s, 9H), 2.33 (s, 3H), 3.9 (qm, $J = 9$ Hz, 2H), 6.0 (s, 1H), 7.1−7.5 (m, 4H); Ar = 4-MeO-C_6H_4, R = Me: $\delta = 0.12$ (s, 9H), 3.79 (s, 3H), 5.68 (s, 1H), 6.88 (dm, $J = 9$ Hz, 2H), 7.35 (dm, $J = 9$ Hz, 2H); Ar = 4-MeO-C_6H_4, R = CH_2CF_3: $\delta = 0.16$ (s, 9H), 3.81 (s, 3H), 3.9 (qm, $J = 9$ Hz, 2H), 5.99 (s, 1H), 6.93 (dm, $J = 9$ Hz, 2H), 7.4 (dm, $J = 9$ Hz, 2H); Ar = β-naphthyl, R = Me: $\delta = 0.14$ (s, 9H), 3.31 (s, 3H), 5.9 (s, 1H), 7.4−7.7 (m, 3H), 7.8−8.0 (m, 4H); Ar = β-naphthyl, R = CH_2CF_3: $\delta = 0.18$ (s, 9H), 4.0 (qm, $J = 9$ Hz, 2H), 6.2 (s, 1H), 7.35−8.05 (m, 7H).

IR measurements of solutions of MeOH, t-BuOH, TFE, and HFIP in CCl_4 or CH_3CN as solvents were performed with a Bruker IFS66 FTIR spectrometer, using 1−5 mm IR-transparent "Infrasil" quartz and 0.5 mm CaF_2 cells.

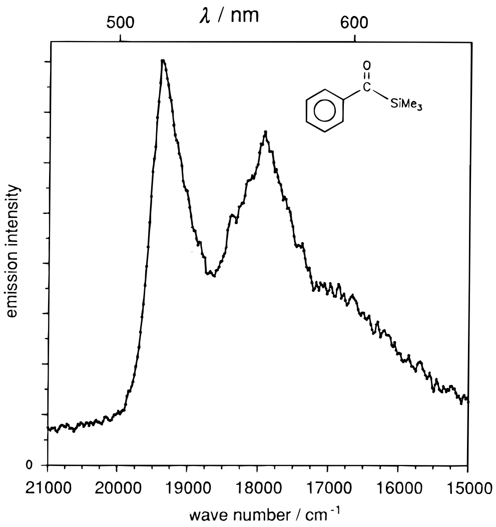

Figure 1. Phosphorescence emission spectrum observed on excitation (λ = 250 nm) of $PhC(O)SiMe_3$ (0.2 mM, OD/cm = 1.55) in a deoxygenated EtOH glass at 77 K.

For the laser flash photolysis experiments we used a Lambda Physik EMG103MSC excimer laser which emitted ≈20 ns, 10−40 mJ pulses of 248 nm light (KrF*). The solutions containing the silanes had optical densities (OD) at 248 nm of ≈1.5/cm which correspond to concentrations of 0.2−0.5 mM. The solutions were flowed (in some cases, after bubbling with oxygen or argon) through the 2 × 4 mm Suprasil quartz cell (flow rates ca. 0.5 mL/min). The light-induced optical transmission changes were digitized in parallel by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73$^+$ computer which also process-controlled the apparatus and on-line preanalyzed the data. Final data analysis was performed on a Microvax I connected to the LSI.

Results and Discussion

1. Photolysis Products. The products of the stationary photolysis of deoxygenated 15 mM solutions of the benzoyltrimethylsilanes 4-$RC_6H_4C(O)SiMe_3$ (**1**, R = H, Me, MeO) in water-free methanol were the mixed acetal 4-$RC_6H_4CH(OMe)$-$OSiMe_3$ (>90%), the acetal 4-$RC_6H_4CH(OMe)_2$, and 4-RC_6H_4-CHO (together ≤ 10%). β-Naphthyl$C(O)SiMe_3$ (**2**) behaved analogously. In TFE, the mixed acetals $ArCH(OCH_2CF_3)$-$OSiMe_3$ and the aldehydes ArCHO were obtained in a molar ratio ≈ 3:2.

The acetals, whose formation is in agreement with previous findings,[8,9] are thought to arise (see later) from the photochemically generated carbenes $ArC^{\cdot}OSiMe_3$ by reaction with methanol. Since "reduction products" $ArCH_2OSiMe_3$ or $Ar(OSiMe_3)$-$CHCH(OSiMe_3)Ar$ were not found, it is concluded that the carbenes do not react by H-abstraction. This indicates that they are in the singlet state.

With the R = MeO system, photolyses in TFE were also performed in the presence of 18−20 mM $Me_4N^+Cl^-$ or n-$Bu_4N^+F^- \times 3H_2O$. It was found that Cl^- had *no* effect on the product ratio, whereas, with F^-, the aldehyde 4-$MeOC_6H_4$-CHO was the main product, and only traces of the mixed acetal 4-$MeOC_6H_4CH(OMe)OSiMe_3$ were detectible (yield ≤ 1%). The production of aldehyde is explained in terms of reaction of the siloxycarbenium ion with F^- (oxygen displacement reaction by F^-, eq 7), see section 5. This reaction is analogous to the F^--induced fragmentation[16] of trimethylsilyl-containing acetals.

2. Phosphorescence Measurements. Deoxygenated solutions of **1** (R = H, Me, MeO) and of **2** (optical density at 250 nm ≈ 1.5 per cm) in ethanol or in *n*-butyronitril at 77 K (where they exist as glasses) were found to phosphoresce when excited with light of 250 nm. As an example, in Figure 1 is shown the phosphorescence spectrum of the parent silane (R = H). There are two peaks, one at 509 nm[17] and a less intense one at 548

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[14] Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373. Brook, A. G., Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102. Picard, J. P. Calas, R.; Donogues, J.; Duffaut, N.; Gerval, J.; Lapouyade, P. *J. Org. Chem.* **1979**, *44*, 420.

[15] Based on HPLC and on their phosphorescence in EtOH glasses[16] at 77 K and their (very weak) triplet−triplet absorption spectra (for a review, see: Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1) in acetonitrile, TFE, or HFIP at room temperature (see Figures 2 and 4).

[16] Lipshutz, B. J.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343.

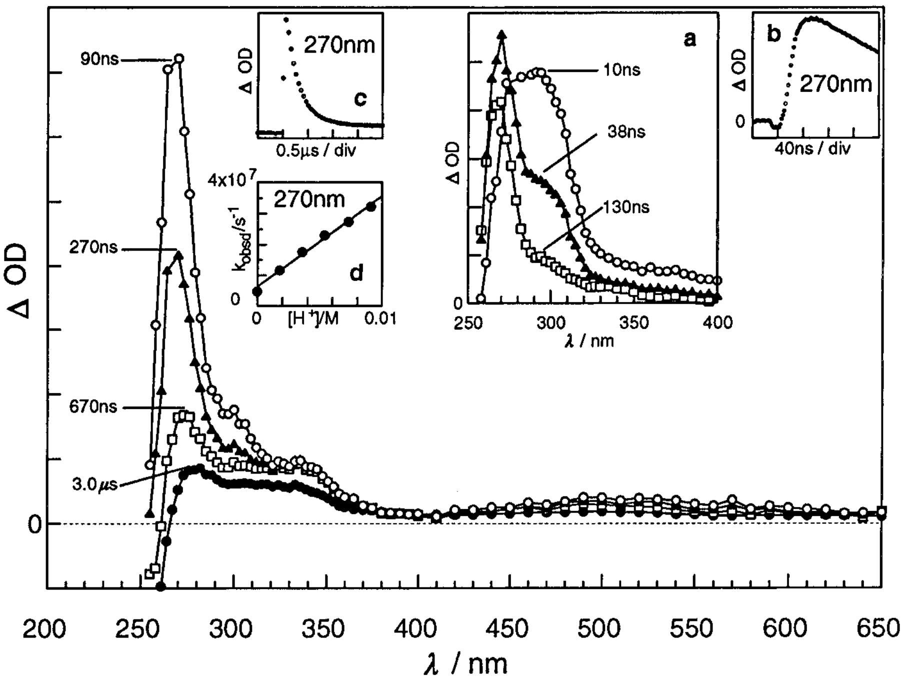

Figure 2. Time-resolved absorption spectra produced on 248 nm photolysis of PhC(O)SiMe$_3$ **1** (0.25 mM) in deoxygenated acetonitrile. The times indicated refer to the situation after the 20 ns pulse. In the insets are shown the carbonyl triplet of **1** with λ_{max} at 290 nm (a), the buildup of the carbene at 270 nm (b), the decay of the carbene at 270 nm (c), and the dependence of k_{obsd} for decay of carbene on [HClO$_4$] (d).

nm, and a shoulder at 600 nm. The shorter wavelength peak (λ_1) corresponds to an energy of the triplet, E_T, of the silane of 56 kcal/mol.[18] On the basis of quenching experiments with isoprene, the triplet energy of the benzoylsilane R = H has been estimated to be ≤ 60 kcal/mol,[10] which is in agreement with our directly measured value.

The phosphorescence lifetime at 77 K, determined by monitoring the decay of the emission intensity at both wavelengths, was found as 0.4 ± 0.1 ms, a value within the range observed for carbonyl triplets.[19] Also in *liquid* ethanol at ≈170 K could emission be seen, which was strongly quenched by oxygen. This is in support of the luminescence originating from the triplet state of the carbonyl compound.

The para-substituted benzoylsilanes also showed phosphorescence[16] in ethanol glasses at 77 K. The λ_{max} values, triplet energies (calculated from λ_1), and lifetimes (τ) are listed in Table 1. It is interesting that the triplet energies of the acyl*silanes* are considerably lower than those (≈74 kcal/mol)[19a] of the corresponding acyl*alkanes*.[20] Low triplet energies of acylsilanes have been noted previously.[9,10]

3. Laser Flash Photolysis (LFP) Experiments in Acetonitrile. a. Identification of Carbenes. The time-resolved absorption spectra observed on 248 nm photolysis of a deoxygenated 0.25 mM solution of the benzoylsilane **1** (R = H) in acetonitrile (AN) are presented in Figure 2. Insets a−c illustrate the observations made during the first 130 ns after the pulse. As seen in inset a, at ≈10 ns, there is a band with λ_{max} at ≈290 nm, which decays very rapidly ($k \approx 6 \times 10^7$ s^{-1}). As this band disappears, a band with $\lambda_{max} \approx 270$ nm grows in (see inset b),[21] indicating that the 270 nm species is the product of the 290 nm species. The 270 nm species decays on a longer time scale (see inset c) with $k = 4.5 \times 10^6$ s^{-1}. This rate is not influenced by the introduction of O$_2$ (8.2 mM) to the solution, demonstrating that the species is probably not a radical or triplet. However, *the species absorbing at 290 nm* shows some reactivity with O$_2$, as concluded from the fact that its lifetime and yield are reduced by 8.2 mM O$_2$. In the presence of O$_2$, the yield of the 270 nm species is also decreased (to 70% of the value in the absence of O$_2$), which supports the idea that the 270 nm species is a product of the 290 nm one.

As seen in the spectrum recorded at 90 ns, in addition to the main band at 270 nm there is a “shoulder” at ≈ 340 nm and a broad band centered around 500 nm. The species responsible for the absorptions at 340 and 500 nm can be efficiently scavenged by O$_2$. It is identified as the triplet of benzaldehyde, whose presence as a thermal decomposition product of **1** is difficult to avoid.[22] As can be seen in Figure 2, the benzaldehyde triplet is longer lived than the species absorbing at 270 nm.

On the basis of its reactivity with O$_2$, the 290 nm species is identified as the triplet of the benzoylsilane **1**; R = H.[23] Its *product*, which absorbs at 270 and at ≈500 nm, is assigned as phenyltrimethylsiloxycarbene **1′** (R = H), formed[9,10] according

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[17] There was also phosphorescence at lower wavelengths, which, based on the authentic emission spectra (Görner, H.; Kuhn, H. J. *J. Phys. Chem.* **1986**, *90*, 5946), is assigned to the corresponding 4-RC$_6$H$_4$CHO present in the sample as impurity.

[18] The triplet energy of acetyltrimethylsilane has been reported[9] to be 61 kcal/mol.

[19] For typical lifetimes of carbonyl triplets at 77 K, see, e.g. (a) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966.

[20] In agreement with the low triplet energies of the acylsilanes is the observation that the triplet of **1** (R = H) is not able to H-abstract from the excellent H-atom donor isopropyl alcohol (used as solvent), as judged by the observability of the triplet of **1** and by the absence of the protonated ketyl radical, which has λ_{max} at 310 nm (strong and narrow band) and at 450 nm (weaker and broader band). This radical was generated by reaction of the acylsilane with e^-_{solv} produced by *radiolysis* of isopropyl alcohol−water mixtures 3:7 (v/v). Inability of the triplet to abstract H from isopropyl alcohol was also observed[9] in the case of acetyltrimethylsilane.

[21] The formation of the 270 nm species *appears* to be faster than the decay at 309 nm. This apparent enhancement of rate is an artefact caused by the almost simultaneously occurring decay of the 270 nm species. This species has a second, very broad band with a center at ≈500 nm.

[22] The spectra in inset a were recorded with a solution containing *less* benzaldehyde than in the case of the main figure.

[23] In agreement with this assignment is the fact that it can also be scavenged by the triplet quencher 1,3-cyclohexadiene: At 1.3 mM 1,3-cyclohexadiene the triplet is barely visible, and the yield of the 270 nm species is reduced to 50%.

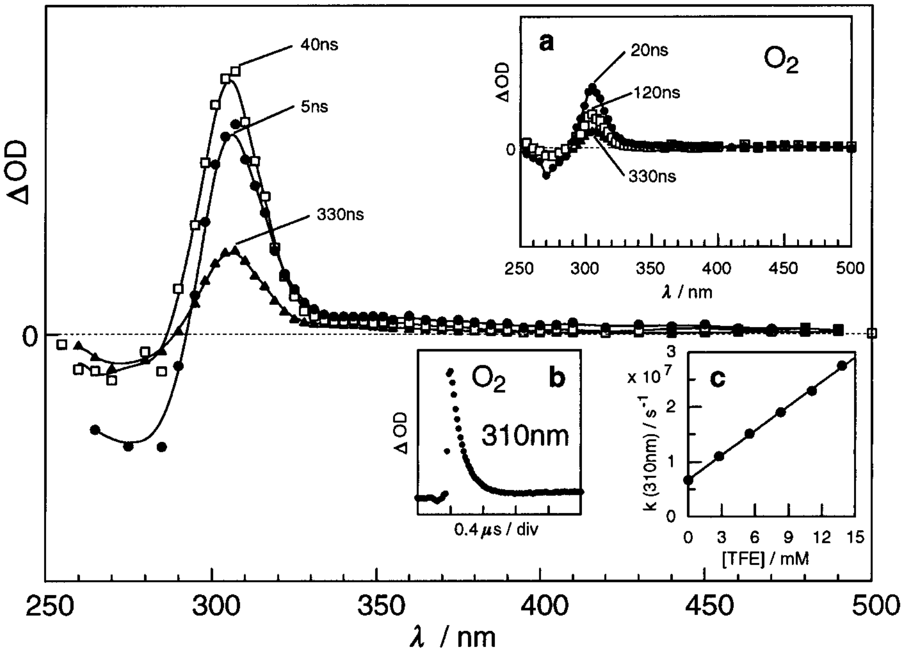

Figure 3. Absorption spectra observed on photolysis of a deoxygenated 0.24 mM solution of **1** (R = MeO) in AN. Recognizable (from the time-dependence of the spectra) is the delayed formation of the carbene (λ_{max} = 310 nm) from the (invisible) carbonyl triplet precursor. In the insets a and b is shown the situation in the presence of 8.2 mM O_2 (the ΔOD scale in inset a is the same as that in the main figure), and in c the effect of TFE on the decay rate of the carbene as monitored at 310 nm.

Table 1. Spectroscopic (and Lifetime) Properties of Acylsilanes and Their Triplets and of Siloxycarbenes

	acylsilane[a]	carbonyl triplet[b]			carbene[c]	
Ar	λ(absorption)/nm; ϵ/M^{-1} cm^{-1}	λ_{max}(emission)/nm	E_T/kcal mol^{-1}	τ	λ_{max}/nm	τ/ns
4-RC_6H_4						
R = H	251; 11370	509; 548	56	0.14 ms;[b,d] 17 ns[c,e]	270	220; 63[a]
R = Me	261; 13070	510; 545	56	0.72 ms;[b,d]d ≤ 15 ns[c,f]	280	170
R = MeO	277; 7070	496; 535	58	2.2 ms;[b,d] ≤ 15 ns[c,f]	310	130
β-naphthyl	254; 26900	496; 520; 555	58		300	260

[a] In cyclohexane at 20 ± 1 °C. [b] In deoxygenated EtOH at 77 K. [c] In deoxygenated acetonitrile at 20 ± 1 °C. [d] Determined via the phosphorescence decay. Error limit 10%. [e] Monitored by the triplet−triplet absorption at ≈300 nm, see text. [f] Based on the absence of a signal attributable to the triplet.

to eq 4.[24] Based on the fact that **1′** (R = H) does not react with O_2, the carbene is in the singlet state.

$$\underset{\mathbf{1}}{4\text{-}RC_6H_4C(O)SiMe_3{}^{T}} \rightarrow \underset{\mathbf{1'}}{4\text{-}RC_6H_4\dot{\text{C}}OSiMe_3} \quad k \approx 6 \times 10^{7}\ s^{-1} \text{ for } R = H \quad (4)$$

From the decay at 290−310 nm and the buildup at 270 nm, the rate constant for the transformation reaction $\mathbf{1}^{T} \rightarrow \mathbf{1'}$ (R = H) is 6×10^7 s^{-1}, which corresponds to a lifetime of the triplet of 17 ns. This measured value in acetonitrile is considerably shorter than the 50−100 ns estimated[10] for CH_2Cl_2 solutions but essentially the same as that (19 ns) deduced[9] for acetyltrimethylsilane in acetone solution.

Results similar to those described for **1**, R = H, were found for the two other benzoylsilanes, R = Me and MeO, and for the β-naphthoylsilane **2**. In all cases the *yields* of carbenes were reduced (see Figure 3) in the presence of O_2, which is interpreted in terms of scavenging of the carbene precursor, the carbonyl triplet, by O_2. However, the *lifetimes* of the carbenes, which decay by first order kinetics to OD levels slightly above those before the pulse (see Figures 2 and 3, insets c and b), were not effected by O_2. The first order decay of carbene can be interpreted as (thermal) regeneration of the acylsilane precursor, since in the absence of carbene traps the optical density returns to almost its original level. The λ_{max} values of the absorptions of the carbenes and of the emissions of the carbonyl triplets and the lifetimes in AN (room temperature) and ethanol (77 K) are collected in Table 1. Concerning the carbenes **1′**, the λ_{max} values *in*crease from R = H to R = MeO, whereas the lifetimes *de*crease in this direction.

b. Reaction of Carbenes with Proton Donors. It was found that the carbenes can be scavenged by compounds containing mobile protons. Addition of increasing concentrations of proton donor led to increasing rates k_{obsd} for decay of carbene and to increasingly negative ΔOD values after completion of the reaction. This indicates that the reversion of carbene into acylsilane (which has absorption at λ_{max} of the carbene) is prevented by the proton donor. The rate enhancement for decay of **1′** (R = H) is shown in Figure 2, inset d, for $HClO_4$, and in Figure 3 for TFE reacting with **1′** (R = MeO).

To obtain quantitative data on the reactivity of the carbenes, i.e., rate constants, the (first order) rates of decay of the carbenes (k_{obsd}) at their λ_{max} values (see Table 1) were monitored as a function of the concentration of the proton donor. With the more acidic proton donors, such as 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP), and $HClO_4$, the observed dependences (see inset d in Figure 2 and inset c in Figure 3) were found to follow the equation $k_{obsd} = k_o + k_{prot}$ [proton donor], where k_o is the rate of decay of the carbene in

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[24] Evidence for photoinduced siloxycarbene formation was also obtained in the case of α,β-epoxysilylketones (Scheller, M. E.; Frei, B. *Helv. Chim. Acta* **1992**, *75*, 69).

Table 2. Rate Constants (M^{-1} s^{-1}) for Reaction of Siloxycarbenes $Ar\ddot{C}OSiMe_3$ with Proton Donors[a] and for Decay in Oxygen-Saturated Acetonitrile at 20 ± 1 °C

		Ar/λ(observation)			
proton donor	pK_a (ROH)[b,c]	C_6H_5/270 nm	4-MeC_6H_4/280 nm	4-$MeOC_6H_4$/310 nm	β-naphthyl/300 nm
H_2O	15.7	9.3×10^{7} [d]	9.2×10^{7} [d]	1.0×10^{8} (60 mM)[e,f]	1.2×10^{8}[d]
CH_3OH	15.5	3.0×10^{8} [d]	2.7×10^{8} [d]	3.8×10^{8} (25 mM)[e,f]	2.2×10^{8}[d]
CH_3CH_2OH	15.9			2.0×10^{8} (17 mM)[e,f]	
$HOCH_2CH_2OH$	15.1	9.1×10^{8} (30 mM)	1.5×10^{9} (20 mM)	3.0×10^{9} (7 mM)	
$CH_3OCH_2CH_2OH$	14.8	1.6×10^{8} (25 mM)[e]	2.6×10^{8} (15 mM)[e]	6.3×10^{8} (14 mM)[e]	
$CH_3OCH_2CH_2OD$		1.2×10^{8} (20 mM)[e]	2.6×10^{8} (20 mM)[e]	6.0×10^{8} (16 mM)[e]	
$ClCH_2CH_2OH$	14.31	1.1×10^{9} [g]		2.0×10^{9} (7 mM)	
Cl_2CHCH_2OH	12.89	2.0×10^{9} [g]		2.1×10^{9} (6 mM)	
Cl_3CCH_2OH	12.24	1.6×10^{9} [g]		2.0×10^{9} (3 mM)	
CF_3CH_2OH (TFE)	12.8	1.5×10^{9}	1.8×10^{9}	1.5×10^{9}	1.5×10^{9}
$(CF_3)_2CHOH$ (HFIP)	9.3	1.2×10^{9}	1.0×10^{9}	1.2×10^{9}	9.6×10^{8}
$(CF_3)_2CHOD$ (HFIP-OD)		1.3×10^{9}		1.2×10^{9}	
CH_3CO_2H	4.75	1.1×10^{9} [g]	1.2×10^{9} [g]	1.0×10^{9} [g]	9.9×10^{8}
CH_3CO_2D[h]		1.1×10^{9} [g]	1.1×10^{9} [g]	1.1×10^{9} [g]	1.0×10^{9}
$HClO_4$		3.0×10^{9}	2.4×10^{9}	2.6×10^{9}	2.0×10^{9}
4-$O_2NC_6H_4OH$	7.15	$\sim 3 \times 10^{9}$			
CH_3CN solvent		4.5×10^{6} [i]	5.8×10^{6} [i]	7.5×10^{6} [i]	3.9×10^{6} [i]

[a] In the case of the linear k_{obsd} vs concentration plots, the error limits are ±10%. In the other cases, the *k* values are approximations based on the low concentration ranges indicated in the parentheses. The *k* values were determined at the wavelengths given. [b] From Dyatkin, B. L.; Mochalina, E. P.; Knunyants, I. L. *Tetrahedron* **1965**, *21*, 2991. [c] From Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795. [d] The k_{obsd} vs [proton donor] plot is curved *upward*. Value reported is from a linear fit in the concentration range 0−0.15 M. [e] The k_{obsd} vs concentration plot is curved *upward*. The value is from a linear fit in the concentration range indicated. [f] Curvature is not very pronounced. [g] At [proton donor] > 10 mM, the k_{obsd} vs concentration plots are curved *downward*. The numbers given are from the linear parts in the low concentration range. [h] The water content of CH_3CO_2D is 2%. [i] Rate constant k_s for carbene decay in spectroscopic grade CH_3CN with a water content <0.1%. Unit s^{-1}.

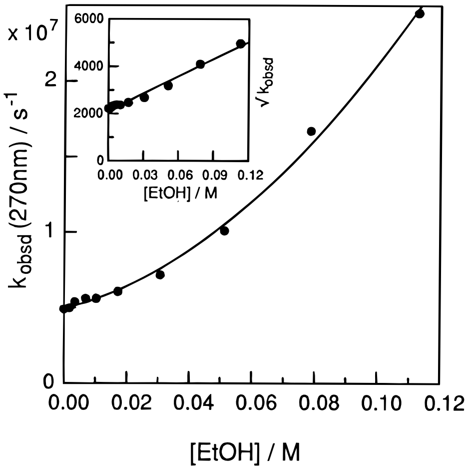

Figure 4. Dependence of k_{obsd} for decay in AN of 1′ (R = H), monitored at 270 nm, on [ethanol]. From the inset it is recognizable that the dependence can be approximated by a parabola.

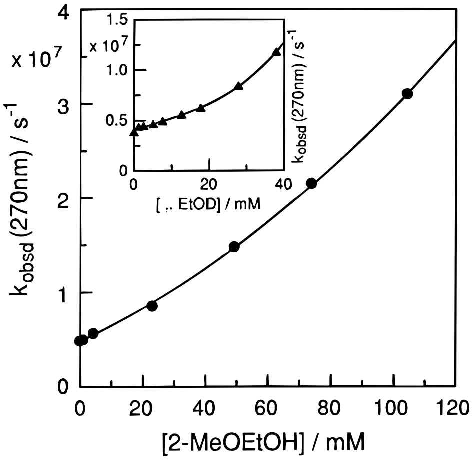

Figure 5. Dependence of k_{obsd} for decay in AN of **1′** (R = H), monitored at 270 nm, on [2-methoxyethanol]. Main figure, ROH; inset, ROD.

the *absence* of the proton donor, and k_{prot} the second order rate constant for reaction of the carbene with the proton donor. In these cases the second order rate constants k_{prot} (see Table 2) are (well) defined. In other cases, such as the reactions of H_2O, methanol, ethanol, or 2-methoxyethanol with the carbenes **1′** and **2′**, the k_{obsd} vs concentration plots are curved *upward* (see Figures 4 and 5 and Table 2). In other cases, such as the 2-chloroethanols (see Figure 6) and acetic acid, the plots are curved *downward*. In these nonlinear cases the numbers given in Table 2 are approximations based on the initial, quasi-linear parts and refer only to the concentration ranges indicated in the footnotes.

In the case of acetic acid, HFIP, and 2-methoxyethanol (see inset Figure 5), the rate constants (listed in Table 2) were also measured for reaction of the carbenes **1′** with the O-*deuterated* molecules. With HFIP, which has a high reactivity ($k \approx 1.2 \times 10^{9}$ M^{-1} s^{-1}), replacement of the alcoholic proton by D has no influence on the rate constant for reaction with **1′** (R = H, MeO). Analogously, O-deuteration does not change the reactivity of acetic acid with **1′** (R = H, Me, MeO). With these proton donors, the kinetic isotope effect, k_H/k_D, is thus 1.0. In the case of 2-methoxyethanol, the reactivity data are less reliable, due to the curvature of the k_{obsd} vs [ ] plots (see Figure 5). However, it appears (see Table 2) that the kinetic isotope effect is small ($k_H/k_D \leq 1.3$).

The rate constants for reaction of $HClO_4$ with **1′** are ≈2.7×10^{9} M^{-1} s^{-1}, which is almost an order of magnitude lower than the diffusion limit in acetonitrile (2×10^{10} M^{-1} s^{-1}).[25] In order to check the possibility that the reactions in this solvent of the highly polarizing (and therefore probably strongly solvated) proton might be *less* than 2×10^{10} M^{-1} s^{-1}, oxygen-saturated (to scavenge any radicals) solutions containing 0.3 mM α- or β-naphthol in acetonitrile were photolyzed with 20 ns pulses of 248 nm laser light. Since the acidity of the electronically excited singlet state of naphthol is larger by seven orders of

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[25] The rate constant for reaction of the related carbene, benzylchlorocarbene, with hydrogen chloride in isooctane has been measured by Liu, M. T. H.; Chateauneuf, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1575, to be 4.7×10^{9} M^{-1} s^{-1}, which is also below the diffusion limit in this solvent (calculated from the viscosity (= 0.345 cp) to be 1.9×10^{10} M^{-1} s^{-1} at room temperature, using the Smoluchovsky equation).

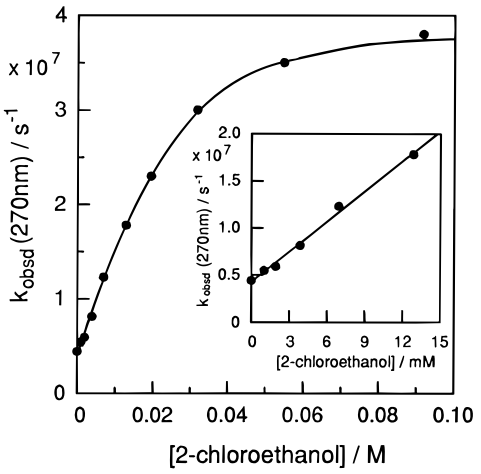

Figure 6. Dependence of k_{obsd} for decay in AN of **1′** (R = H), monitored at 270 nm, on [2-chloroethanol]. In the inset it is shown that at low [2-chloroethanol] the dependence is essentially linear.

magnitude than that of the ground state,[26] photolysis leads to deprotonation which results in a rapid increase in the conductance of the solution, followed by a slow (second order) decrease to the prepulse level, this process being due to ion recombination (protonation of the naphtholate anion). It was found that by adding $HClO_4$ to the solution, the rate of conductance decrease after the pulse increased dramatically, with the kinetics changing from second to first order. The k_{obsd} values for conductance decrease were found to follow the equation $k_{obsd} = k_0 + k_{H^+}[H^+]$, from which the protonation rate constants, k_{H^+}, resulted as 4×10^{10} and 3.6×10^{10} M^{-1} s^{-1} for α- and β-naphtholate, respectively.[27,28] These values are clearly *above* the diffusion limit for reaction of neutrals (2×10^{10} M^{-1} s^{-1}), but they are in line with the numbers calculated[29] for ionic reactants of opposite charge. From these numbers it is evident that rate constants for proton transfer reactions in acetonitrile are *not* "intrinsically" below diffusion control. The absence of a kinetic isotope effect in the case of the reactions of HFIP and acetic acid with the carbenes **1′** and of acetic acid with **2′** is thus probably *not* due to these reactions being diffusion controlled at $\approx 1 \times 10^9$ M^{-1} s^{-1}.[30] In agreement with this conclusion is the observation that in the case of 2-methoxyethanol, where the rate constants are only $(2-6) \times 10^8$ M^{-1} s^{-1} (see Table 2), i.e., certainly below diffusion control, there is also little difference between the O−H and O−D systems.

While the reaction mechanism for weakly acidic alcohols is not very clear at the moment (see, however, discussion in section 6), conclusive evidence is available for stronger acids. When 4-nitrophenol was used as the proton donor, the reaction with **1′** (R = H) resulted in the production of the 4-nitrophenolate anion, as judged by its characteristic spectrum with λ_{max} at 380 nm. The conclusion is thus that the reaction involves proton transfer. Due to partly overlapping spectra, the rate constant could not be determined with a high degree of precision, but the value is large ($\approx 3 \times 10^9$ M^{-1} s^{-1}, Table 2).

4. LFP Experiments in TFE and HFIP. Formation and Absorption Bands of Carbenium Ions. If the reaction between the carbenes and the proton donors proceeds by proton transfer, carbenium ions are the products. If it is desired to directly detect these species, the reaction should be conducted such that the carbenium ions are formed (a) rapidly and (b) in a non-nucleophilic environment. Conditions (a) and (b) are both fulfilled by working in acidic and non-nucleophilic solvents such as TFE and HFIP. In Figure 7 are shown the time-resolved absorption spectra recorded on 248 nm photolysis of **1**, R = MeO, in TFE. At ≈90 ns after the pulse, a species characterized by a band with $\lambda_{max} = 355$ nm is observed.[31] In the region 250−310 nm, there is a decrease of OD which is caused by depletion of parent ($\lambda_{max} = 277$ nm, see Table 1). The 355 nm species decays with first order kinetics (see inset b), the rate ($k = 2.0 \times 10^5$ s^{-1}) being insensitive to O_2. As this species disappears, the absorbance at ≈300 nm increases (reflecting product formation, isosbestic point at 305 nm). The rate of decay is strongly accelerated by nucleophiles such as N_3^- (see inset c) or MeOH (see inset d). On the basis of its nucleophilic behavior and its nonreactivity with O_2, the 355 nm species is identified as the cation **1′**H^+, formed by protonation of the carbene **1′** (R = MeO), see eq 5.

Analogous observations were made in the case R = H, where the species detected (identified as the cation **1′**H^+, R = H) had λ_{max} at 305 nm. Its decay rate (1.0×10^7 s^{-1}) is much larger than that measured for R = MeO (2.0×10^5 s^{-1}). A rate much lower than that in TFE (1.0×10^7 s^{-1}) is observed in the less nucleophilic[32] solvent HFIP (1.0×10^4 s^{-1}). On this basis, the decay of the cation is assigned to reaction with solvent (rate constant k_s). As in the case of R = MeO, the rate is not influenced by oxygen but very strongly by nucleophiles such as alcohols, ethers, and anions. The experimentally observed rate k_{obsd} for decay of the species follows in many cases the equation $k_{obsd} = k_s + k_{Nu}$[nucleophile], with k_{Nu} being the second-order rate constant for reaction with nucleophile. The bimolecular electrophilic reactivity thus characterized (see Table 3) is in support of the species being a cation, the phenyltrimethylsiloxycarbenium ion (R = H), formed by protonation by HFIP (or TFE) of the carbene, eq 5:

$$\underset{\mathbf{1'}}{4\text{-}RC_6H_4\dot{C}OSiMe_3} + R'OH \rightarrow \underset{\mathbf{1'H^+}}{4\text{-}RC_6H_4CH^+OSiMe_3} + R'O^- \quad (5)$$

$$\underset{\mathbf{1'H^+}}{4\text{-}RC_6H_4CH^+OSiMe_3} + R'OH \xrightarrow{k_s} 4\text{-}RC_6H_4CH(OSiMe_3)OR' + H^+ \quad (6)$$

$$R' = (CF_3)_2CH,\ CF_3CH_2$$

The rate of formation of the carbenium ion from the carbene can be estimated if it is assumed that the rate constant for reaction 5 in neat HFIP (=9.5 M) is the same as that measured (1.2×10^9 M^{-1} s^{-1}, Table 2) in acetonitrile. The result corresponds to a lifetime of the carbene in HFIP of 90 ps. Since the observed rate of formation of the cation is much smaller,

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(26) For a review, see: Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

(27) An analogous approach to determine the rate constant for reaction of H^+ with an amine (as a respresentative of a *neutral* reaction partner) was unsuccessful.

(28) In aqueous solution, the rate constant for reaction of H^+ with α-naphtholate anion is 5.9×10^{10} M^{-1} s^{-1} (Schuler, R. H. *J. Phys. Chem.* **1992**, *96*, 7169).

(29) See McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S. Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009, and ref 37.

(30) The rate constant for reaction in isooctane of acetic acid with benzylchlorocarbene is[25a] 1.0×10^9 M^{-1} s^{-1}.

(31) The weak, broad band at ≈400 nm, which is absent in the presence of O_2 (see inset a), is due to the triplet of $4\text{-}MeOC_6H_4CHO$, which is present as an impurity.

(32) For quantitative data on the solvolyzing power and the nucleophilicity of HFIP, see: Schadt, F. L.; Schleyer, P. v. R.; Bentley, T. W. *Tetrahedron Lett.* **1974**, *27*, 2335. Bentley, T. W.; Clewellyn, G. *Progr. Phys. Org. Chem.* **1990**, *17*, 121.

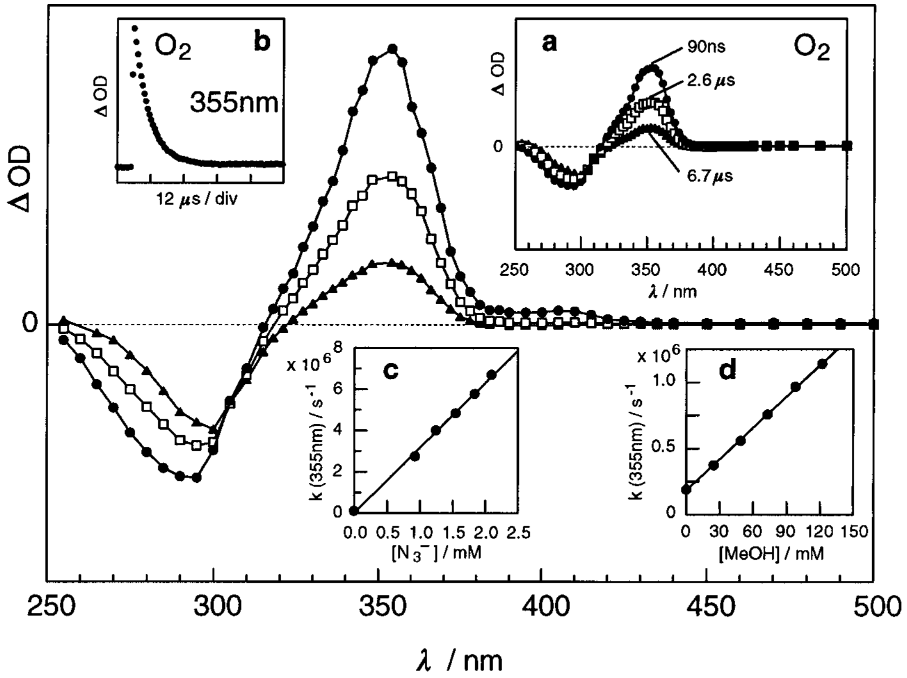

Figure 7. Time-resolved absorption spectra observed on photolyzing a deoxygenated 0.16 mM solution of **1** (R = MeO) in TFE: circles, 90 ns; squares, 2.6 μs; triangles, 6.7 μs after the pulse. In inset a is shown the situation in the presence of O_2, in b the decay of the carbenium ion as monitored at 355 nm (the decay rate is exactly the same in the absence of O_2). The acceleration of the cation decay by N_3^- and by MeOH is shown in c and d.

i.e., ≈6 × 10^7 s^{-1}, this means that the rate-determining step in the formation of the carbenium ion is the transformation of the triplet into carbene (eq 4) and not the protonation of the latter.[33]

When the other silanes, **1**, R = Me and **2**, were photolyzed in the solvents HFIP or TFE, transient spectra of the corresponding carbenium ions **1′**H$^+$ and **2′**H$^+$ were observed. The *lack* of reactivity with radical scavengers such as O_2 and the *high* reactivity with typical nucleophiles such as alcohols, ethers, and anions are indicative of carbocations. The spectroscopic and reactivity data of all the cations studied are collected in Table 3. In the series of the α-trimethylsiloxyphenyl carbenium ions **1′**H$^+$, the substituent in the para position has a strong effect on the absorption band of the cation: λ_{max} increases from 305 nm for R = H to 355 nm for R = MeO. For the β-naphthyl system, λ_{max} = 350 nm.

5. Reactivities of Carbenium Ions and Solvent Effects. Due to the short lifetime (≈100 ns) in TFE of **1′**H$^+$ (R = H), its reactivity was studied mainly in the less nucleophilic solvent HFIP. The other cations, **1′**H$^+$ (R = Me, MeO) and **2**H$^+$, were investigated in TFE. Concerning the rate constants for decay of cation by reaction with solvent, k_s, those for **1′**H$^+$ decrease from 1 × 10^7 to 2 × 10^5 s^{-1} and from 1 × 10^4 to 1 × 10^2 s^{-1} in the solvents TFE and HFIP, respectively, i.e., approximately by two orders of magnitude, in going from R = H to R = MeO (see Table 3). This decrease in reactivity reflects the stabilization of the carbenium ions by the electron-donating substituents. It is interesting that the reactivity of the 4-tolyl- is similar to that of the β-naphthyl carbenium ion, both with respect to reaction with solvent (k_s) and with the various nucleophiles (k_{Nu}, see below). The rate constants for solvent decay for the cations ArCH$^+$OSiMe$_3$ are interesting in comparison with previously reported values for ArCH$^+$Me.[34] For Ar = 4-MeOC$_6$H$_4$ there is only a small kinetic stabilizing effect associated with replacing Me with OSiMe$_3$, but as the aromatic becomes less electron donating the difference becomes larger. In solvolytic studies of benzyl and 4-methoxybenzyl cations, analogous effects were reported for a wide range of α substituents.[34] Concerning the effect of solvent, it is evident that the lifetimes of the cations in HFIP are longer than in TFE by about three orders of magnitude, as already mentioned for the case of **1′**H$^+$, R = H.

The cations were reacted with a series of nucleophiles (Nu), alcohols, ethers, and anions. For obtaining the second-order rate constants k_{Nu}, the rate of decay of the cation, k_{obsd}, was measured at its λ_{max} as a function of [Nu]. In the case of the solvent TFE, k_{obsd} vs [Nu] plots (for reaction of **1′**H$^+$ (R = Me and MeO) and of **2′**H$^+$) were linear and had k_s as the intercept. The k_{Nu} values obtained from the slopes of such plots are presented in Table 3 in columns 3−5. It is evident that the reactivities of water and methanol are similar. Among the alcohols, there is a clear *de*crease in reactivity from methanol to *tert*-butyl alcohol, independent of the nature of the cation.[35] Since the basicity/nucleophilicity of the alcohols is not very different, the decrease of reactivity in the observed direction is probably due to steric crowding in forming the C−O bond between the cation and the oxygen of the alcohol in the reaction in which the mixed acetal[9] is formed. Among the ethers tetrahydrofuran (THF) and 1,4-dioxane, the latter is in all cases much less reactive, which reflects its considerably lower nucleophilicity,[36] caused by the −I effect of the second oxygen in the ring.

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[33] An analogous conclusion was reached[10] concerning the rate determining step in the formation at −40 °C of ylid from triplet **1** (R = H) and pyridine via **1′**.

[34] Amyes, T. L.; Stevens, I. W.; Richard, J. P. *J. Org. Chem.* **1993**, *58*, 6057.

[35] Similar differences were seen between the alcohols in their reactivity with other carbocations, see: (a) Kobayashi, S.; Zhu, Q. Q.; Schnabel, W. *Z. Naturforsch.* **1988**, *436*, 825. (b) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648. (c) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, 7710. (d) Verbeek, J.-M.; Stapper, M.; Krijnen, E. S.; van Loon, J.-D.; Lodder, G.; Steenken, S. *J. Phys. Chem.* **1994**, *98*, 9526.

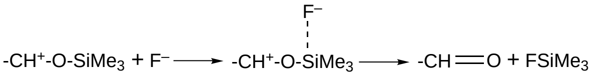
[36] This is deduced from the lower basicity of dioxane, cf.: Searles, S.; Tamres, M. Basicity and Complexing Ability of Ethers. In The Chemistry of the Ether Linkage; Patai, S., Ed.; Interscience: London: 1967; pp 243−308.

Table 3. Rate Constants k_{Nu} ($M^{-1}\ s^{-1}$) for Reaction of Carbenium Ions with Nucleophiles (Nu) at 20 ± 1 °C

	p-$RC_6H_4CH^+OSiCMe_3$; solvent			β-naphthyl $CH^+OSiCMe_3$	Ph_2CH^+; solvent		
Nu	R = H; HFIP $\lambda_{max} = 305$ nm	R = Me; TFE $\lambda_{max} = 315$ nm	R = MeO; TFE $\lambda_{max} = 355$ nm	solvent TFE $\lambda_{max} = 350$ nm	HFIP[a] $\lambda_{max} = 430$ nm	TFE[b] $\lambda_{max} = 435$ nm	CH_3CN[c] $\lambda_{max} = 435$ nm
TFE	$1 \times 10^{7\ d}$	$2 \times 10^{6\ e}$	$2 \times 10^{5\ e}$	$4 \times 10^{6\ e}$		$3.0 \times 10^{6\ d}$	$2.5 \times 10^{6\ f}$
HFIP	$1 \times 10^{4\ e}$	$7 \times 10^{3\ g}$	$1 \times 10^{2\ g}$	$1 \times 10^{3\ g}$	$5 \times 10^{3\ g,h}$		
H_2O	$1.4 \times 10^{6\ i}$	3.8×10^7	9.5×10^6	4.2×10^7	$(1-2) \times 10^{3\ i}$	1.1×10^6	1.2×10^8
MeOH	$2.8 \times 10^{6\ i}$	5.7×10^7	7.8×10^6	4.9×10^7	$5 \times 10^{5\ i}$	1.0×10^7	1.2×10^9
EtOH	$2.0 \times 10^{6\ i}$	3.7×10^7	6.3×10^6	3.9×10^7	$3 \times 10^{5\ i}$	1.3×10^7	8.5×10^8
2-PrOH	$8.1 \times 10^{5\ i}$	2.0×10^7	2.3×10^6	2.3×10^7	$(1-2) \times 10^{5\ i}$	7.8×10^6	3.1×10^8
t-BuOH	$2.1 \times 10^{5\ i}$	8.6×10^6	6.8×10^5	1.4×10^7	$9 \times 10^{4\ i}$	3.2×10^6	6.9×10^7
$HOCH_2CH_2CH_2OH$	$4.5 \times 10^{6\ i}$	3.9×10^7	1.6×10^6	6.8×10^7	$6 \times 10^{5\ i}$		
THF	$2.1 \times 10^{6\ i}$	3.0×10^7	2.2×10^6	3.9×10^7	4.9×10^4	*k*	*k*
1,4-dioxane	$4 \times 10^{4\ i}$	4.0×10^6	5.0×10^5	3.2×10^6	2.2×10^4	1.3×10^6	
F^-	3.2×10^7	7.1×10^8	1.7×10^8	9.4×10^8	3.8×10^7	1.9×10^8	2.0×10^{10}
Cl^-	8.4×10^6	1.8×10^8	2.1×10^7	1.3×10^8	8.1×10^8	1.9×10^9	2.0×10^{10}
Br^-	3×10^6	1.3×10^8	2.2×10^7	5.3×10^7	3.8×10^9	5.9×10^9	2.1×10^{10}
I^-	1.4×10^6	*l*	1.5×10^7	*l*	8.6×10^9	7.5×10^9	1.9×10^{10}
N_3^-	2.6×10^8	4.9×10^9	3.1×10^9 $1 \times 10^{7\ n}$	5.4×10^9 $5.2 \times 10^{7\ n}$	5.6×10^8	5.3×10^9	$2.1 \times 10^{10\ m}$

[a] Cation produced by photoheterolysis of Ph_2CHOH (ref 35). [b] Cation produced from 1,1,2,2-tetraphenylethane radical cation by C−C fragmentation (Faria, J. L.; Steenken, S. Unpublished results). [c] Data from ref 32c. [d] Rate (k_s/s^{-1}) in TFE as solvent. [e] k_s, units s^{-1}. [f] Solvent rate (k_s) in CH_3CN. [g] Rate (k_s/s^{-1}) in HFIP as solvent. [h] Data from Faria, J. L. [i] The k_{obsd} vs concentration plots are curved upwards, see text. The reported second order *k* values are therefore upper limits, obtained from the tangent in the concentration range 0−0.25 M. [k] Reaction is reversible (Bartl, J.; Mayr, H.; Steenken, S. Unpublished results). [l] No effect on I^- on decay of cation seen up to 0.018 M. [m] This work. [n] In HFIP as solvent.

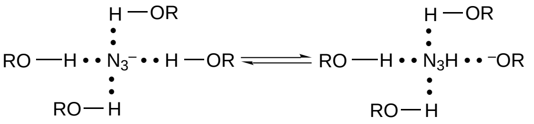
A very interesting phenomenon is that the halides react with the cations **1′**H$^+$ and **2′**H$^+$ in the reactivity order $F^- > Cl^- > Br^- > I^-$, i.e., in a way *opposite* to the halide *nucleophilicities*. In order to test whether this “inversion” of normal reactivity has to do in any way with the fluoroalcohol solvents, the benzhydryl cation Ph_2CH^+ was produced by 248 nm photolysis in HFIP of Ph_2CHOH[37] or in TFE of tetraphenyloxirane[38] or of 1,1,2,2-tetraphenylethane[39] and reacted with the nucleophiles monitoring the cation decay at 430−435 nm. The results are presented in columns 6 and 7 of Table 3, together with analogous data obtained[35c] in acetonitrile. It is clear that in the solvents TFE and HFIP the reactivity of the halides with Ph_2CH^+ is governed by their nucleophilicity, with the classical order $I^- > Br^- > Cl^- > F^-$.[40] The opposite behavior of **1′**H$^+$ and **2′**H$^+$ is thus an intrinsic property of these cations and not of the solvents. Their higher reactivity with the smaller halides can be explained by assuming (initial) reaction *not* with the cationic center C_α, but with the silicon atom. Particularly for Hal = F, an oxygen-displacement reaction (eq 7) could be thermodynamically more favorable than attachment to C_α, due to the large Si−F bond energy.



$$\text{-CH}^+\text{-O-SiMe}_3 + F^- \longrightarrow \text{-CH}^+\text{-O-}\overset{F^-}{\text{SiMe}_3} \longrightarrow \text{-CH=O} + \text{FSiMe}_3 \quad (7)$$

The formation of aldehyde as main product in the presence of F^- (see section 1) could be in support of eq 7. However, Cl^- does not seem to react analogously, based on the fact (see section 1) that Cl^- has no effect on the product yield. Therefore, the apparent decrease in the reactivity from Cl^- to I^- may result from an increasing degree of reversibility of the ion combination reaction.[41]

Due to its exceptionally high reactivity, the strong nucleophile N_3^- has been widely used to trap carbocations (“azide clock”).[42] In fact, azide is the most reactive nucleophile with **1′**H$^+$ and **2′**H$^+$. With $k_{N_3^-} \approx (3-5) \times 10^9\ M^{-1}\ s^{-1}$, the reaction in TFE is diffusion controlled.[43] However, in HFIP the rate constant is only 2.6×10^8 (for **1′**H$^+$, R = H), 1×10^7 (for **1′**H$^+$, R = MeO), and $5.2 \times 10^7\ M^{-1}\ s^{-1}$ (for **2′**H$^+$). Since the rate constant for diffusion in HFIP is $4.2 \times 10^9\ M^{-1}\ s^{-1}$,[37,44] these low numbers (and the similarly low number for Ph_2CH^+, see Table 3) are remarkable. A possible explanation involves decrease of the effective nucleophilicity of the strong base N_3^- (pK_a(N_3H) = 4.75)[45] by hydrogen-bonding (quasi-protonation) from the acidic O−H group of HFIP.



$$\text{RO—H} \cdot\cdot \underset{\text{RO—H}}{\overset{\text{H—OR}}{N_3^-}} \cdot\cdot \text{H—OR} \rightleftharpoons \text{RO—H} \cdot\cdot \underset{\text{RO—H}}{\overset{\text{H—OR}}{N_3H}} \cdot\cdot {}^-\text{OR} \quad (8)$$

This concept of deactivation by hydrogen bonding to the nucleophile is also applicable to reaction of cation with alcohols and with water. E.g., in the case of Ph_2CH^+, the k_{Nu} values are lower by the factor 40−100 in TFE than in acetonitrile (where there is no such deactivation), and they are even lower in HFIP.[46] Other examples are **1′**H$^+$, where the k_{Nu} values for water or alcohol or ether, measured in TFE, *in*crease in going

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(37) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924.

(38) Kilian, J.; Kirmse, W. Unpublished results. The cation is produced via Ph_2C:.

(39) The formation of the cation proceeds via the radical cation (Faria, J. L.; Steenken, S.; McClelland, R. A. Unpublished results.

(40) The fact that in acetonitrile there is no difference in the k_{Nu^-} values for the different halides (see column 8 of Table 3) is due to the reactions being diffusion controlled. For a discussion of diffusion control in carbocation reactions, see ref 29 and ref 37.

(41) Reversibility has been found in the addition reaction of Ph_3C^+ with Br^-, but not with Cl^- or F^- (McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023). It is interesting that the rate constants for reaction in TFE of the cations with N_3^- ($k = (3.1-5.4) \times 10^9\ M^{-1}\ s^{-1}$, see Table 3) are diffusion controlled, which contrasts with the low values for I^-. This is an argument in favor of reversibility in the reaction with I^-, since I^- and N_3^- have similar nucleophilicities, but differ vastly with respect to leaving group properties. A reviewer suggested that it is also possible that the *forward* rate constants decrease in a way reflecting the decreasing stability of the C−X bond in going to X = I.

(42) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689. Amyes, T. L.; Richard, J. P. *J. Chem. Soc. Chem. Commun.* **1991**, 200 and references therein.

(43) The diffusion rate in TFE, whose viscosity at 25 °C is 1.780 centipoise (from a) Murto, J.; Heino, E.-L. *Suomen Kemistilehti B* **1966**, *39*, 263), is calculated with the Smoluchovsky equation to be $3.7 \times 10^9\ M^{-1}\ s^{-1}$.

(44) Calculated with the Smoluchovski equation from the viscosity of HFIP of 1.579 centipoise at 25° C (from a) Murto, J.; Kivinen, A.; Lindell, E. *Suomen Kemistilehti B* **1970**, *43*, 28).

(45) Cotton, F. A.; Wilkinson, G. Advances in Inorganic Chemistry; John Wiley and Sons: New York, 1980; p 421.

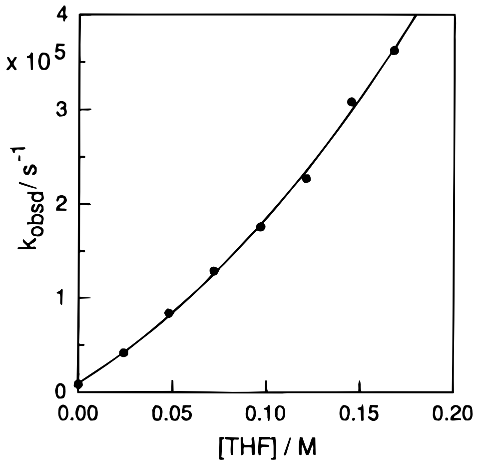


Figure 8. Dependence on [THF] of k_{obsd} for decay of **1′**H^+ in HFIP.

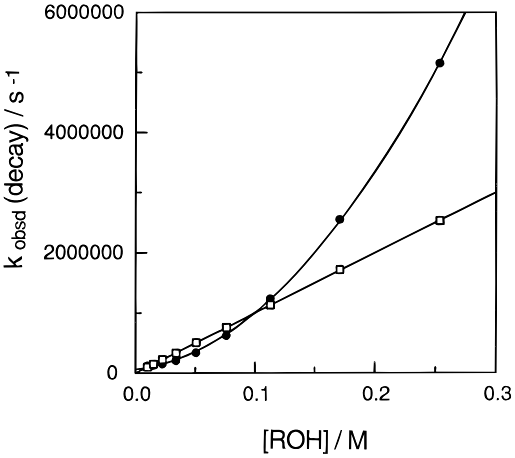


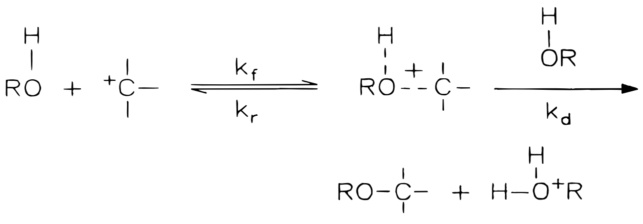
Figure 9. Results of the computer simulation of eq 9 in terms of k_{obsd} for cation decay as a function of [ROH]. The reaction with solvent (eq 6) was included, taking $k_s = 10^5\ s^{-1}$. It was assumed that $k_f = 10^8\ M^{-1}\ s^{-1}$ and $k_d = 10^9\ M^{-1}\ s^{-1}$. The rate constant k_r was varied: The squares are for $k_r = 10^7$, the circles for $10^9\ s^{-1}$.

from R = MeO to the less stabilizing Me, and a further increase is expected on going to R = H. However, for R = H the values are considerably *lower*, since the *k* values now refer to reaction in the much stronger H-donor HFIP.[47]

With respect to the solvent HFIP, a particularly interesting phenomenon is that for reaction of cations **1′**H^+ (R = H) and Ph_2CH^+ with water, the alcohols, and ethers, the k_{obsd} values for cation decay are *not* proportional to [Nu] but follow the relation $k_{obsd} = k_s + k[Nu]^n$, with $n = 1.2-2$.[48] As an example for this behavior is shown the system **1′**H^+ with THF (Figure 8).

The case $n > 1$ suggests that more than one molecules of Nu are involved in the reaction with the cation. Nonlinear dependences of k_{obsd} on [Nu] have been previously observed for reaction of Ph_2CH^+ with methanol, ethanol, and 2-propanol in 1,2-dichloroethane.[49] For an explanation, di- or oligomerization by intermolecular hydrogen bonding of the alcohols in this very nonpolar, nonprotic solvent was invoked.[49−51] In contrast, in an alcoholic solvent such as HFIP, solute−solute association by hydrogen bonding is very unlikely, due to heavy competition by H-bonding with solvent. In fact, the decrease in cation reactivity with Nu in going from acetonitrile via TFE to HFIP, as described above, is evidence for strong solute−*solvent* interaction. An even stronger argument *against* oligomerization being the reason for the curvature is the fact that in the case of the ethers THF and 1,4-dioxane, the k_{obsd} vs [Nu] plots are also "curved upward" (see Figure 8 and Table 3).

Obviously, dimerization via H-bonds, as assumed in the case of alcohols, is not possible with ethers. This type of mechanism is therefore not applicable. For this reason, a mechanism that does not involve (rely on) di- or oligomerization is required to explain the curvature in the k_{obsd} vs [Nu] plots. We therefore propose an alternative concept which is based on the very weak *basicity* of HFIP. In the reaction of a cation C^+ with ROH (R = H, alkyl) yielding C-OR, a proton is released which has to be transferred to a base. In many cases the solvent will be able to serve as this base. However, if the solvent has a very low basicity, C−O bond formation will not go to completion unless a second ROH takes part serving as the base.[52] The most likely way as to how this can happen is shown below:



(9)

The mechanism involves an equilibrium between the cation and the alcohol and their addition product,[53] the O-protonated ether, with k_f being the second-order rate constant for adduct formation and k_r the first order one for reversal into reactants. The reverse step corresponds to what happens in the H^+-catalyzed hydrolysis of ethers. Decomposition of the protonated ether into product (*second*-order rate constant k_d) requires transfer of the proton to a second alcohol molecule.

In order to test whether this mechanism gives rise to the experimentally observed curved k_{obsd} vs [Nu] plots, computer simulations were performed. In addition to eq 9, the reaction of cation with solvent (rate constant k_s) was taken into account and assumed to be reversible with a ratio of 10:1 for the forward and reverse directions. The dependence on time of the concentration of the cation was then calculated for various concentrations of Nu, while the ratio [Nu]:[cation] was always kept ≥100, such that pseudo-first order conditions were fulfilled with respect to the reaction of the cation (and of the adduct, eq 9). The rate constants k_f, k_r, and k_d were then systematically varied (k_s was taken as $10^5\ s^{-1}$), and the resulting calculated concentration-time profiles were analyzed in terms of first order kinetics for the decay of the cation[54] (as is done with the *experimentally* obtained concentration-time profiles). An im-

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(46) The values in HFIP are upper limits, due to the upward curvature of the k_{obsd} vs [] plots. For a discussion see text.

(47) There is also a polarity change in going from HFIP ($\epsilon = 16.6$)[43a] to TFE ($\epsilon = 26.7$)[44a] to acetonitrile ($\epsilon = 37.5$).

(48) A similar observation has been previously made in HFIP.[11,12]

(49) Sujdak, R. J.; Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 4875.

(50) The crucial assumption involved in this concept is that the dimers or oligomers, formed by hydrogen bonding between the oxygens, are *more nucleophilic* than the monomeric alcohols where the only nucleophilic center of the molecule, the oxygen atom, is *not* involved in hydrogen bonding.

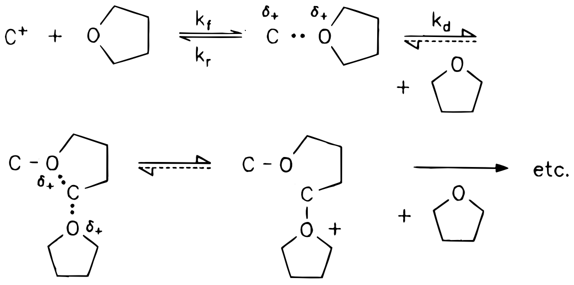
(51) An analogous concept was later applied to reactions of carbenes with alcohols, see ref 67.

(52) Interestingly, it was already noted by Dorfman[49] that in the case of participation of a second alcohol molecule, the leaving group from the protonated ether is not the proton but an alkoxonium ion, a "bonded, stabilized state of the proton".

(53) Evidence for an equilibrium is the observation that the decay of the cations in HFIP on the microsecond timescale does not *quite* go to the zero-line in the *absence* of nucleophiles, but it does in their presence, due to depletion of the cations by reaction with the nucleophiles.

portant result of the simulations is that the lifetime of the complex has to be very short, in order to get upward curved k_{obsd}−[ ] dependences. E.g., if it is assumed that $k_f = 10^8$ M^{-1} s^{-1} and $k_d = 10^9$ M^{-1} s^{-1}, k_r must be $> 10^7$ s^{-1}, smaller values giving *linear* dependences. This means is that quasi-*ter*molecularity is required in order for curved-up behavior to be seen: With a complex which is too long-lived, the condition of quasi-simultaneity of the interaction of *two* Nu molecules with cation is not fulfilled. The computer calculations thus show that the experimental data are compatible with the proposed mechanism. Another relevant result is that curved-*down* k_{obsd} vs [Nu] plots were not achievable on the basis of eq 9.

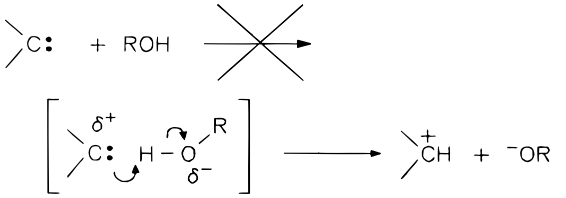
The mechanism explains the upward curved k_{obsd} vs [Nu] plots also for THF and 1,4-dioxane. In addition to the equilibrium postulate,[55] it invokes the participation of a second ether molecule which reacts as a Lewis base, i.e., by nucleophilic attack at the (incipient) carbocationic center produced by ring-opening of the oxonium ion (nucleophilic assistance by the second ether molecule). This is essentially the mechanism of cationic polymerization of ethers.[56] The difference between eqs 9 and 10 is that in eq 9 the second molecule acts as a Brönsted base, whereas in eq 10 it functions as a Lewis base.



(10)

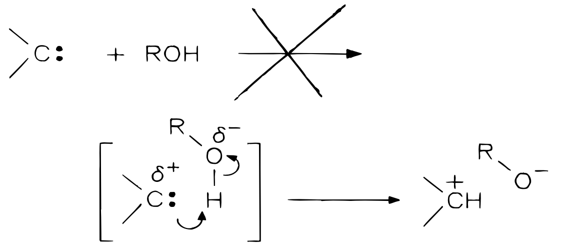
A prediction that can be made on the basis of the mechanisms 9 and 10 is that curved k_{obsd} vs [Nu] dependences should also be observed in solvents *more* basic than HFIP provided the cations are *less* electrophilic (more "stable", i.e., longer lived in the usual nucleophilic solvents) than the siloxycarbenium ions discussed here.[57] This situation is, however, not yet reached with Ph_2CH^+ in TFE (see Table 3 for some rate constants).

6. Comments on the Reactivity of Carbenes with Alcohols. As already mentioned in section 3b, in the reaction in acetonitrile of the carbenes **1′** with the proton donors 2-methoxyethanol, HFIP, and acetic acid, O-deuteration does not decrease the reactivity of the donors. Analogous observations have been made previously. E.g., with 9-xanthylidene, $k_H/k_D = 1.13$ for reaction with *tert*-butyl alcohol-OH/OD),[58] for 3,6-dimethoxyfluorenylidene, $k_H/k_D = 1.17$ for reaction with MeOH/OD,[59] for $(MeO)_2C$:, $k_H/k_D = 1.0$ for reaction with AcOH/AcOD,[60] and for **1′** (R = H), $k_H/k_D = 1.6$ and 1.9 for reaction with MeOH(OD) and EtOH(OD),[10] respectively.[61,62] Since, as reported in section 3b, the reactions of the siloxycarbenes with the proton donors are very probably *not* diffusion-controlled (*certainly* not in the case of 2-methoxyethanol), a kinetic isotope effect of 1 *excludes* a linear transition state for transfer of the proton[63] fom O to the carbenic C,[64] i.e.



(11)

However, if the carbene approaches in a direction orthogonal to the O−H bond as in eq 12, an isotope effect close to 1 is expected:



(12)

As seen from the entries in Table 2, the k_{prot} values for TFE, HFIP, and $HClO_4$ (obtained from the slopes of the linear k_{obsd} vs [proton donor] plots) are essentially invariant of the nature of the carbene.[66] Since the stability of the corresponding carbenium ions (as deduced from their lifetimes, see section 5

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(54) The exponential fit to the *calculated* concentration-time profiles was always very good, and the same is true for most of the experimentally *observed* ones.

(55) The reversibility of cation reaction with ether has been shown for the reaction of Ph_2CH^+ with THF (Bartl, J. Dissertation, Universität zu Lübeck, Germany, 1990).

(56) For a discussion of relevant mechanistic problems see, e.g.: Kirmse, W., Jansen, U. *Chem. Ber.* **1985**, *118*, 2607 and references cited therein.

(57) For a given cation and ROH, with increasing basicity of the solvent, ROH will be replaced by solvent molecules. This leads to a decrease (loss) of curvature in the k_{obsd}-[] dependences.

(58) Lapin, S. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4243. The rate constants were determined by an *indirect* method.

(59) Chuang, C.; Lapin, S. C.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4238.

(60) Moss, R. A.; Shen, S.; Wlostowski, M. *Tetrahedron Lett.* **1988**, *29*, 6417.

(61) Kinetic isotope effects *larger* than those quoted above have also been reported in the literature. E.g., in ref 60 is given $k_H/k_D = 3.3$ for reaction of $(MeO)_2C$: with MeOH(D). However, the rate constants were taken from k_{obsd} vs [MeOH(D)] plots with *negative* intercepts[60] (which physically make no sense). This indicates that the k_{obsd}-[MeOH(D)] dependences are really *curved upward*, as seen in the case of MeOH(OD) reaction with the closely related carbene MeOC⁚Me, where k_H/k_D (as taken from the low concentration range) appears to be 1.[60] The curved plots indicate a dependence of the reactivity on alcohol concentration, see text. Concerning the k_H/k_D numbers of 1.6 and 1.9 for **1′** (R = H),[10] these were determined by an *indirect* method, possibly at a single concentration of alcohol. If the dependence on concentration of the reactivity was different for MeOH and MeOD, this would lead to concentration-dependent k_H/k_D numbers. A further example is the MeOC⁚F reaction with AcOH(OD) for which a k_H/k_D value of 1.95 was reported.[68b] It is not, however, clear to which extent k_{obsd}-[AcOH(OD)] dependences were determined.

(62) As an explanation for the low kinetic isotope effects, the argument was invoked that the reactions were (close to) diffusion controlled.[58−60] However, the reported rate constants are lower by the factor ≥10 than k_{diff}, as calculated using the Smoluchovsky equation.

(63) Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry, 2nd ed.; Harper and Row: New York, 1981; pp 205−212. See also, e.g.: Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

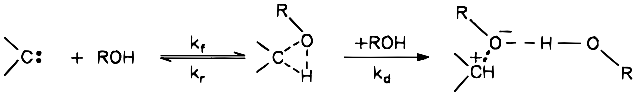
(64) The solvent kinetic isotope effect for protonation on C of CN^- is 4.5 (Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117). A further example is the protonation by H_2O of the electron adduct of guanosine where $k_H/k_D = 8.0$ (Candeias, L. P.; Wolf, P.; O'Neill, P.; Steenken, S. *J. Phys. Chem.* **1992**, *96*, 10302). For a review on solvent kinetic isotope effects, see: Kresge, A. J.; More O'Ferrall, R. A.; Powell, M. F. Solvent Isotope Effects, Fractionation Factors and Mechanisms of Proton Transfer Reactions. In Isotopes in Organic Chemistry; Buncel, E., Lee, C. C., Eds.; Elsevier: Vol. 7, pp 177−273.

(65) Obviously, an ylid mechanism is excluded due to the absence of reasonable ways by which an ylid could be converted into the experimentally observed carbenium ion.

(66) However, in the case of ethylene glycol and 2-methoxyethanol, there is an increase by the factor 3−4 in going from R = H to R = MeO (see Table 2), indicating a *small* contribution of proton transfer to C: in the transition state.

and Table 3) increases considerably in going from **1**, R = H to R = MeO and to **2**, the independence of the k_{prot} values on the Brönsted basicity of the carbenes indicates that in the transition state for carbene protonation a carbenium ion nature is only weakly developed. This essentially excludes eq 12. The independence on the nature of R also excludes an ylide-type transition state where there would be *negative* charge on the carbenic carbon. However, the experimental observations are understandable in terms of the carbene attacking not H but the O−H bond ("insertion") since in such a transition state there is little, if any, ion character (see eq 13).

A further aspect of mechanistic importance already referred to in footnote 61 has to do with the *curved* k_{obsd} vs [proton donor] plots. In Table 2 it is reported that these plots for the reaction of the siloxycarbenes **1′** and **2′** with, e.g., water, methanol, and ethanol are curved *upward*, i.e., the reactivity of the proton donor *in*creases with its concentration (see also Figures 4 and 5). This type of phenomenon was first reported for reaction of the carbenes $4\text{-RC}_6\text{H}_4\ddot{\text{C}}\text{Cl}$ with *methanol* in acetonitrile and isooctane,[67] and a number of similar cases has since become known.[68,69] The upward curvature was interpreted on the basis of oligomer formation by hydrogen bonding between the alcohol molecules and assuming a *higher* reactivity of the oligomers than of the monomer to an extent overcompensating the concomitant decrease of concentration.[70,71] Concerning the highly polar solvent CH_3CN which is an excellent proton acceptor, dimerization by H-bond formation is not very likely, due to the strong competition by H-bonding to the solvent (the nitrogen of CH_3CN). In order to test this idea, IR measurements of solutions of MeOH and of t-BuOH as model alcohols (and also of TFE and HFIP) in CH_3CN were performed. In contrast to the situation in the solvent CCl_4, where the alcohol di- and oligomers are clearly visible (for MeOH at 3523 (dimer) and 3342 cm^{-1} (oligomer), monomer at 3643 cm^{-1}),[72] in CH_3CN only the solvated monomer (for MeOH at 3541 cm^{-1}) was seen, and absolutely no evidence for dimer or oligomer formation was found up to alcohol concentrations of 0.4 M. Thus, in the solvent CH_3CN, di- or oligomerization of the alcohols mentioned above does not take place. For explaining the "upward behavior" observed with the less acidic alcohols, a mechanism is therefore suggested which contains the same formalism as the reaction mechanism proposed for carbocations and nucleophiles, i.e., an equilibrium formation of a complex between the reactants followed by assistance by a second molecule of reactant, whereby a (contact) ion pair is possibly involved:



(13)

It is assumed that the decomposition rate k_d of the complex is determined (the carbenium remaining the same) by the stability of the (incipient) alkoxide anion for which the pK_a of the alcohol is a measure. For *weakly* acidic alcohols, complex decomposition needs assistance by a second alcohol which stabilizes the (incipient) anion by H-bonding. Comparison of this concept with that involving the cation reaction with alcohols (eq 9) shows that the mechanisms, although formally analogous, are chemically reciprocal: with the cations it is the *nucleo*philicity, with the carbenes the *electro*philicity of the alcohols which is the determining factor. The fact (see Table 2) that the k_{obsd} vs [alcohol] plots for **1′** and **2′** are *linear* for highly acidic alcohols such as TFE and HFIP can be explained by assuming that k_r is small or negligible and k_d large, in contrast to the case of the less acidic alcohols and water.[73] With the weaker proton donors, the proton transfer from O to the carbene C: is assumed to be reversible and to go to completion only if a second proton donor solvates the (incipient) alkoxide anion.[74,75] Scheme 13[76] is able to account for the different curvatures observed for different alcohols by allowing for different sets of rate constants for k_f, k_r, and k_d. The mechanism is also in agreement with the observation that the reactivity of methanol is lower in acetonitrile than in isooctane: In acetonitrile the alcohol O−H protons are tied up in hydrogen bonding to the nitrile group[67] and therefore only partially available for protonation of the (incipient) alkoxide.[77,78]

Possibly the strongest, though indirect support for the reversible complex formation hypothesis comes from work on diphenylmethylene[79] and fluorenylidene,[80] where it was shown that the reactions of these carbenes with alcohols are not one-step processes[81] and that, specifically, there is an equilibrium in which the carbene is regenerated.[82] Furthermore, on the basis

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[67] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549. Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, 1543.

[68] (a) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563. (b) Du, X.-M.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krogh-Jespersen, K.; La Villa, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920. (c) Vasella, A.; Briner, K.; Soundarajan, N.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 4741. (d) Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Wlostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341. (e) Reference 60.

[69] Interestingly, the corresponding plots for *tert-butyl alcohol* were curved *downward*.[67]

[70] This concept is analogous to that proposed by Dorfman[49] for reactions of alcohols with carbocations.

[71] The crucial assumption involved in this concept is that the dimers or oligomers, formed by hydrogen bonding between the oxygens, are *more electrophilic* than the monomeric alcohols where the only electrophilic center of the molecule, the OH proton, is *not* involved in hydrogen bonding. For methanol, the enhancement of reactivity required to explain the experimental results on the basis of this concept corresponds to a factor ≈150.[67] Cf. ref 50.

[72] For information on alcohol dimer and oligomer formation, see, e.g.: Frange, B.; Abboud, J. L. M.; Benamou, C.; Bellon, L. *J. Org. Chem.* **1982**, *47*, 4553. For the effects of this on the philicity of alcohols, see Huyskens, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 2579.

[73] Linear behavior with acidic alcohols has also been observed with other carbenes, see ref 68c.

[74] In the case of glycols, the electrophilic assistance by the second OH group can occur *intra*molecularly. This may be a reason for the linear k_{obsd}-[] plots and for the considerably enhanced reactivity of ethylene glycol compared to the *more* acidic 2-methoxyethanol (see Table 2), whereby the statistical factor (ethylene glycol has *two* OH) has to be taken into account. It may also be interesting that in the case of **1′** (R = MeO), ethylene glycol is more reactive than the much more acidic HFIP.

[75] The dimerization hypothesis[49,67] involves *simultaneous*, whereas Schemes 9 and 13 are based on *consecutive* interaction with two reactants of the same type. The idea that the function of the second alcohol is to stabilize by hydrogen bonding the alkoxide resulting from the first alcohol (rather than to increase the acidity of the first one) can, of course, also be applied to the dimerization hypothesis. An essential difference between the two ideas lies in the equilibrium assumed with the consecutive interaction concept.

[76] For the computer calculations, the reversal of the carbene into acylsilane was taken into account. The most important condition to be fulfilled for obtaining curved-up k_{obsd}-[] plots is a short lifetime of the complex, i.e., k_r should be $\geq 10^8\ \text{s}^{-1}$.

[77] However, in order to explain the curve-down dependences (see Figure 6 and Table 2), association phenomena (*without* overcompensatory reactivity enhancement) have to be invoked.

[78] A case has been reported[68d] where the k_{obsd}-[] plot, after an initial curved-*up* part, curves *down*. This can be explained by the effects of di- and oligomerization overcompensating electrophilic assistance by the second alcohol molecule.

[79] Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23.

[80] Zupancic, J. J.; Grasse, P. B.; Lapin, S. C.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 1471.

of the results with fluorenylidene, it was suggested[80] that there was some "communication" from one alcohol to another in the reaction sequence and that observed kinetic isotope effects "might arise from changes in solvation or association equilibria of the alcohol". These general ideas can be visualized in terms of Scheme 13. On this basis, a kinetic isotope effect can be envisaged as arising under conditions where k_d is rate determining, specifically, the proton transfer from the second alcohol to the incipient alkoxide anion, involving a linear transition state RO^-..H-OR.

Summary and Conclusions

The carbenes $4\text{-}RC_6H_4\ddot{C}OSiMe_3$ (R = H, Me, MeO) and β-naphthyl$\ddot{C}OSiMe_3$, formed by rearrangement from the triplet states of the corresponding acylsilanes $ArC(O)SiMe_3$, have been characterized spectroscopically and by their reactivity with proton donors, particularly alcohols. In the solvents TFE and HFIP, the carbenes give rise to α-siloxycarbenium ions, whose spectroscopic properties and electrophilic reactivity have been described. With respect to reaction with the halides, there is an inversion of the classical order, i.e., F^- being *more* reactive with the carbenium ions than I^-. In the weakly basic solvent HFIP, the reaction with alcohols and ethers is suggested to proceed via reversible formation of a cation−nucleophile adduct which proceeds to product (ether and H^+ or secondary cation) upon assistance by a second alcohol molecule which serves as the proton (or cation) acceptor.

Concerning the mechanism of carbene reaction with ROH in CH_3CN, the observed kinetic isotope effects close to 1 and a weak dependence of protonation rates on cation stability indicate an "early" transition state with little proton transfer from ROH to carbene, and, correspondingly, little charge development. With alcohols less acidic than TFE the protonation of the carbenes is suggested to proceed via reversible formation of a carbene−alcohol adduct which decomposes into product by interaction with a second alcohol molecule.

Acknowledgment. We thank Marion Stapper for her competent technical help and J. L. Faria for letting us use some of the rate constants for reaction of Ph_2CH^+ determined by him (see Table 3). M.G. thanks the Deutsche Forschungsgemeinschaft for a scholarship (DFG-Ste 474/1-1).

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(81) See also, Warner, P. M.; Chu, I. S. *J. Am. Chem. Soc.* **1984**, *106*, 5366; *J. Org. Chem.* **1984**, *49*, 3666.

(82) In the work of Schuster (ref 80), the alcohol is considered a nucleophile with respect to fluorenylidene. However, on the basis of LFP experiments (unpublished results), the reaction leads to 9-fluorenyl *cation*, i.e, the alcohol acts as an electrophile. As already noted by Schuster, a difference of this type in the mechanism does not, however, invalidate his conclusion as to the *reversibility* of the reaction between carbene and alcohol.