

Nucleophile-Assisted Cleavage of Benzyltrialkylsilane Cation Radicals

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Abstract: The cation radicals of benzyltrialkylsilanes have been generated using photoinduced electron transfer and characterized using transient absorption spectroscopy. Absolute rate constants for nucleophile-assisted C–Si bond cleavage have been determined, for different nucleophiles in different solvents and with different substituents on the phenyl ring. The short lifetime ($<10^{-9}$ s) of the parent benzyltrimethylsilane cation radical in acetonitrile was unambiguously shown to be due to a rapid nucleophile-assisted bond cleavage, with the solvent acting as the nucleophile. Even in less polar solvents, such as dichloromethane, the lifetime of benzyltrimethylsilane cation radical is quite short (ca. 20 ns) unless trace amounts of water, which acts as an efficient nucleophile, are removed. Consistent with the nucleophile-assisted cleavage mechanism for the benzyltrialkylsilanes, sterically-demanding substituents on silicon decrease the rate constant for cleavage by as much as 4 orders of magnitude, depending upon the nucleophile. Similarly, increasing steric crowding on the nucleophile also decreases the rate constant, although smaller changes in the rate constants are observed. Electron-donating substituents (4-methyl and 4-methoxy) on the phenyl group also lead to a substantial decrease in the rate constant for cleavage of the cation radicals. When measurements are performed in the least nucleophilic solvent and under conditions that minimize contributions from adventitious nucleophiles, the lifetimes of the cation radicals of the benzyltrialkylsilanes can be so long that the rate of pseudo-first-order decay can not be accurately determined. If the cation radicals undergo unimolecular C–Si bond cleavage (i.e., not nucleophile-assisted) under these conditions, the rate constant for this process is estimated to be less than 10^4 s⁻¹.

I. Introduction

The oxidative cleavage of organosilanes and related compounds has been the subject of numerous investigations in recent years.¹ Examples of reactions that have been studied include electron transfer initiated substitutions of benzylsilanes,^{2,3} alkylsilanes,⁴ disilanes,⁵ and enol silyl ethers⁶ and also reactions of tin and germanium compounds.^{2e,4b,7} The mechanism of the bond cleavage reactions has been the subject of considerable discussion. One interesting suggestion is that the cleavage

reaction could occur via a nucleophile-assisted process, with the solvent acting as the nucleophile for sufficiently reactive cation radicals.^{2m,3} We recently proposed that for benzyltrialkylsilane cation radicals ($1^{+\bullet}$) the cleavage reaction does, in fact, proceed via this mechanism, with solvents such as acetonitrile acting as the nucleophile (eq 1).³

On the basis of gas phase thermodynamic cycle calculations, the C–Si bond dissociation energy for benzyltrimethylsilane cation radical was predicted to be ca. 30 kcal/mol,^{3a} which would suggest a large barrier to unimolecular cleavage. The rate constant for fragmentation for this particular cation radical in

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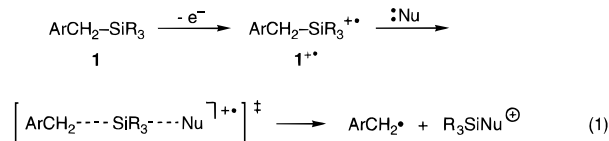
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acetonitrile was estimated to be ca. $1 \times 10^9 \text{ s}^{-1}$, which was taken as strong support for the $\text{S}_{\text{N}}2$ mechanism (eq 1).^{3a}

Direct experimental evidence for this mechanism was obtained for (4-methoxybenzyl)trialkylsilane cation radicals.³ Using time-resolved nanosecond absorption spectroscopy, it was shown that the lifetimes of the silane cation radicals decreased in the presence of a variety of added nucleophiles. Second-order rate constants for reaction between the cation radicals and the nucleophiles were sensitive to steric effects. From these and related experiments, it was clearly demonstrated that the cleavage reaction for (4-methoxybenzyl)trialkylsilane cation radicals occurred via reaction with the solvent, acetonitrile. Evidence that the $\text{S}_{\text{N}}2$ mechanism might be general has also been obtained from product studies of allylsilane photo-oxidations.^{4b} Similarly, product studies suggest that disilane cation radicals undergo nucleophile-assisted cleavage.^{5a}

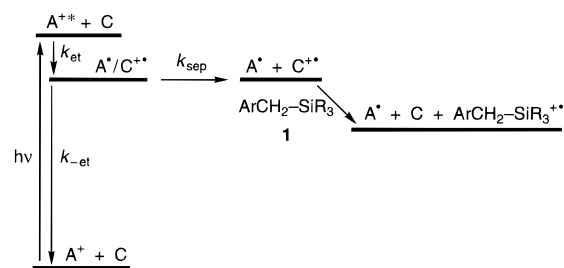
In our original work, the primary evidence in favor of the $\text{S}_{\text{N}}2$ mechanism for the parent benzyltrimethylsilane cation radical came from thermokinetic arguments based on the gas phase C—Si bond dissociation energy. However, it was recently suggested that a unimolecular $\text{S}_{\text{N}}1$ mechanism may be possible in this case, since the *solution phase* bond dissociation energy for the cation radical of benzyltrimethylsilane might be considerably less than the gas phase value.^{4a} In addition, it was noted that nucleophile-assisted cleavage need not be invoked to explain the product distributions observed in the photoinduced electron transfer reactions of some alkyl- and benzylsilanes with tetracyanobenzene.^{4a} The cation radical of the parent benzyltrimethylsilane has not been observed directly in transient absorption experiments, and thus, no direct kinetic evidence regarding the mechanism of its cleavage has yet been obtained. As discussed above, the lifetime of the cation radical was previously estimated to be ca. 1 ns in acetonitrile (the fragmentation rate is estimated to be ca. $1 \times 10^9 \text{ s}^{-1}$)—considerably shorter than the 4-methoxy analogues—and too short-lived to be detected in our original nanosecond transient absorption experiments.^{3a} The shorter lifetime of the parent compound could be because the $\text{S}_{\text{N}}2$ reaction is faster with acetonitrile than for the 4-methoxy derivatives or because the $\text{S}_{\text{N}}1$ reaction is faster than the $\text{S}_{\text{N}}2$ reaction in this case.

The $\text{S}_{\text{N}}2$ cleavage reaction is interesting because formally it represents the addition of a nucleophile to a one-electron σ bond. Although the addition of nucleophiles to π organic cation radicals has been very well studied,⁸ these additions to σ bonds in cation radicals are much less well-known.^{9,10} In addition to this general interest, it is obviously of crucial importance to

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Scheme 1



know whether the σ bond cleavage reaction of a cation radical occurs via an $\text{S}_{\text{N}}2$ or an $\text{S}_{\text{N}}1$ mechanism, in order to design systems which undergo efficient cleavage. Despite its obvious importance, however, the generality of the $\text{S}_{\text{N}}2$ mechanism has not been properly established, since direct experimental evidence has only been obtained for two cleavage reactions of cation radicals in addition to those of the silanes.^{2a-c,3,6a,9a,b}

Because of the issues raised here, we have further investigated the cleavage mechanisms of organosilane cation radicals. Herein we describe experiments designed to test whether the $\text{S}_{\text{N}}2$ mechanism operates under normal conditions for the parent benzyltrialkylsilanes. We also describe experiments which generalize and broaden the scope of the nucleophile-assisted cleavage mechanism. Some of the data discussed here have been communicated previously.^{3a,b}

II. Results and Discussion

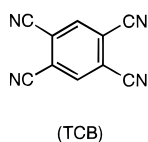
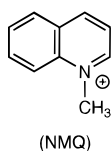
A. Experimental Approach. The clearest method for determining whether a cation radical cleavage occurs via nucleophilic assistance is to measure the rate constant for the bimolecular reaction of the suspected nucleophile with the cation radical and compare this with the rate constant for unimolecular cleavage of the cation radical. Transient absorption spectroscopy using nanosecond-pulsed laser excitation represents an ideal technique for performing these kinetic measurements. For absolute rate studies of cation radicals, cosensitized photooxidation¹¹ has proven to be a useful technique. This is illustrated in Scheme 1 for a positively charged electron acceptor, A^+ , and a cosensitizer, C. Irradiation of A^+ generates the excited state $\text{A}^{+\bullet}$, which reacts with C via exothermic electron transfer, k_{et} , to generate the $\text{A}^*/\text{C}^{+\bullet}$ geminate radical/cation radical pair. The oxidation potential of the cosensitizer is chosen so that diffusional separation, k_{sep} , competes efficiently with return electron transfer, $k_{-\text{et}}$, resulting in a high yield of separated ion radicals. The separated $\text{C}^{+\bullet}$ then oxidizes the silane $\text{ArCH}_2\text{-SiR}_3$ (**1**) to generate the silane cation radical $\text{ArCH}_2\text{-SiR}_3^{+\bullet}$. It is ensured that $\text{A}^{+\bullet}$ reacts with C, rather than with **1**, by using a cosensitizer concentration (ca. 0.1–1.0 M) that is much higher than the concentration of the silane (ca. 10^{-3} – 10^{-2} M). When the oxidation potential of C is higher than that of **1**, the secondary electron transfer from **1** to $\text{C}^{+\bullet}$ occurs with a rate constant close to the diffusion-controlled limit. The concentration of the silane has to be high enough to ensure both that its cation radical is formed more rapidly than it decays and also that $\text{C}^{+\bullet}$ reacts with the silane rather than with other potential reactants in the solution.

Most photoinduced electron transfer reactions are performed in polar solvents to facilitate separation of the photogenerated

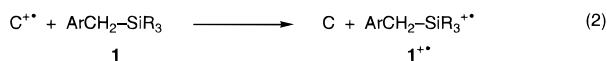
(10) Deprotonation of cation radicals may be viewed as nucleophilic cleavage of a σ bond. For example, see: (a) Anne, A.; Fraoua, S.; Hapiot, P.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 7412. (b) Baciocchi, E.; Giacco, T. D.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290. (c) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 8778. (d) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646.

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anion radicals and cation radicals.¹² In the present studies, however, experiments had to be performed in solvents with lower nucleophilicities than those of most commonly used polar solvents, such as acetonitrile and methanol. For this reason, most of the experiments described here made use of a positively charged electron acceptor (A^+ in Scheme 1). In this case the geminate pair consists of a neutral radical and a cation radical, $A^{\bullet}/C^{+\bullet}$,¹³ compared to the anion radical/cation radical pair which is formed when a neutral acceptor is used. Separation of the $A^{\bullet}/C^{+\bullet}$ pair occurs efficiently even in moderately polar solvents due to the lack of an electrostatic barrier which characterizes the diffusional separation of anion radical/cation radical pairs.^{3c} *N*-Methylquinolinium (NMQ) salts were used for the majority of the experiments. The high oxidizing power of the NMQ excited state ($E_{\text{red}}(S_1) = 2.7$ V vs SCE¹⁴) permits the use of a high oxidation potential cosensitizer such as toluene. A cosensitizer with high oxidizing power was required because of the relatively high oxidation potential of the unsubstituted benzylsilanes (e.g., 1.78 V vs SCE for benzyltrimethylsilane^{3a}). In addition, a neutral electron acceptor was required for some experiments, and in these cases, 1,2,4,5-tetracyanobenzene (TCB) was found to be useful.

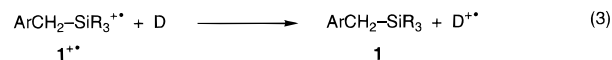


The silane cation radicals are detected by transient absorption spectroscopy. In addition to the silane cation radical, a reduced acceptor (either A^{\bullet} or $A^{-\bullet}$, depending upon the sensitizer) is formed and will also absorb. For the NMQ-sensitized reactions, one method for distinguishing the absorbances of the cation radical from those of the reduced sensitizer is their sensitivity to dissolved oxygen. The reduced form of NMQ reacts with oxygen with a rate constant close to the diffusion controlled limit (presumably due to electron transfer to form superoxide, $O_2^{-\bullet}$), whereas the cation radicals exhibit undetectable reaction with oxygen. Under ideal circumstances, the cation radicals can also be characterized by their electron transfer reactions. The silane cation radicals $1^{+\bullet}$ should be formed at the same rate that $C^{+\bullet}$ is reduced by **1** (i.e., the absorbance growth due to $1^{+\bullet}$ should correspond to the decay of $C^{+\bullet}$ (eq 2)).

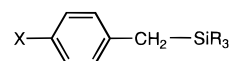


Also, when donor compounds, D, which have lower oxidation potentials than those of **1** are added to solutions with sufficiently

long-lived $1^{+\bullet}$, the approximately diffusion-controlled reaction of $1^{+\bullet}$ with D should occur and a grow-in of $D^{+\bullet}$ should be observed at the same rate at which $1^{+\bullet}$ decays (eq 3).



As discussed above, the first part of the present work deals with the mechanism of cleavage of the parent benzylsilane cation radicals. Benzyltrialkylsilanes containing alkyl substituents with different steric bulk at silicon (**1a–c**) are used to probe the mechanism. In the second part, the scope of the reactivity of nucleophiles with silane cation radicals is explored by including the *para*-substituted silanes **1d** and **1e**.



	X	R
1a	H	CH ₃
1b	H	CH ₂ CH ₃
1c	H	CH(CH ₃) ₂
1d	CH ₃	CH ₃
1e	OCH ₃	CH ₃

B. Benzyltrialkylsilane Cation Radicals. If the cleavage of the benzyltrialkylsilane cation radicals occurs via a nucleophile-assisted mechanism, then on the basis of the previous work on the 4-methoxyphenyl derivatives,^{3a} it was anticipated that their cation radicals would be longer lived when relatively non-nucleophilic solvents were used and also when the silicon was substituted with sterically demanding groups. Our intention was to test this by measuring the absolute lifetimes of the silane cation radicals. However, previous work had indicated that the lifetime of the parent benzyltrimethylsilane was only ca. 1 ns in acetonitrile,^{3a} which was too short for direct detection using nanosecond transient absorption spectroscopy. Therefore, our initial efforts were directed toward determining conditions under which the benzyltrialkylsilane cation radicals lifetimes were long enough to be characterized with this technique.

1. Identification of the Silane Cation Radicals. Using NMQ hexafluorophosphate/toluene-sensitized oxidation of benzyltriisopropylsilane (**1c**), transient absorptions were observed in argon-saturated dichloromethane solution which decayed on a time scale of several microseconds and had an absorption maximum at ca. 540 nm. The anticipated transient species were the benzyltrialkylsilane cation radical (**1c⁺**) and the reduced NMQ, *N*-methylquinolyl radical (NMQ[•]). The absorption maximum of the NMQ[•] is at ca. 550 nm¹⁵ (i.e., consistent with the observed transient absorptions). A contribution of **1c⁺** to the absorptions could be easily demonstrated, however, by the effect of dissolved oxygen, as illustrated in Figure 1. In oxygen-purged solution, a short-lived species was observed with a lifetime of ca. 30 ns, which is assigned to NMQ[•]. The fast decay is due to reaction of the NMQ[•] with oxygen. A longer-lived species decaying on a microsecond time scale was also observed in the oxygen-purged solutions, which is assigned to **1c⁺**. Both the short-lived and the longer-lived species were observed at all of the wavelengths which were monitored, indicating that the absorption spectrum of **1c⁺** is coincidentally similar to that of NMQ[•]. An absorption spectrum was obtained

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(14) Calculated as the singlet excitation energy (3.53 eV) minus the reduction potential (−0.85 V vs SCE) (values determined for *N*-methylquinolinium perchlorate). Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204.

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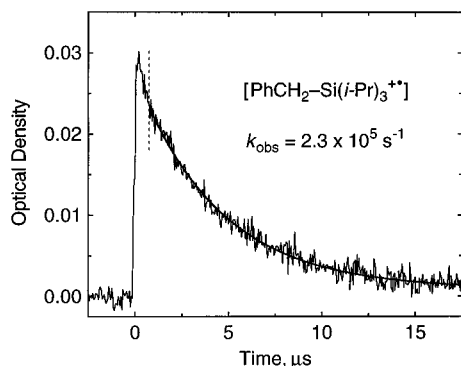


Figure 1. Time-resolved absorption decay observed at 550 nm for excitation of *N*-methylquinolinium (NMQ) hexafluorophosphate with toluene as the cosensitizer in the presence of benzyltriisopropylsilane (**1c**) in oxygen-purged dichloromethane solution. Most of the decay is due to the cation radical of the silane. A fast component at early times (to the left of the dashed line and not included in the fitting) is due to reaction of the *N*-methylquinolyl radical with oxygen. The contribution of *N*-methylquinolyl radical is small on this time scale because of its short lifetime (ca. 30 ns).

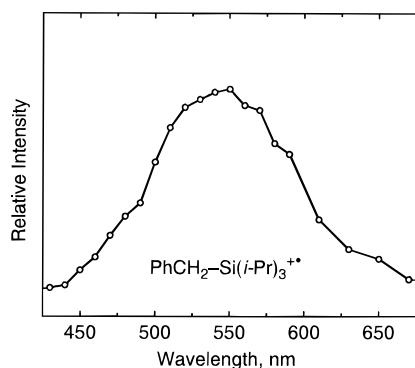


Figure 2. Transient absorption spectrum observed for excitation of *N*-methylquinolinium (NMQ) hexafluorophosphate with toluene as the cosensitizer in the presence of benzyltriisopropylsilane (**1c**) in oxygen-purged dichloromethane solution. The spectrum was recorded 1.5 μ s after the pulse and is due to the silane cation radical **1c**⁺.

for **1c**⁺ by measuring the signal size at different analyzing wavelengths, after the decay of NMQ[•]. A maximum is observed at ca. 540 nm, as shown in Figure 2.

The assignment of the 540 nm transient to the cation radical **1c**⁺ was confirmed by measurements of its electron transfer reactions. Experiments were performed in argon-purged dichloromethane with concentrations of **1c** from 10^{-4} to 4×10^{-3} M. Under these conditions, grow-in of the 540 nm transient could be clearly observed. The slope of a plot of the pseudo-first-order rate constant for the grow-in vs the concentration of **1c** (plot not shown) gave a bimolecular rate constant of 8.4×10^9 M⁻¹ s⁻¹, consistent with oxidation of **1c** by toluene cation radical to give **1c**⁺ (eq 2). Experiments were also performed with a fixed concentration of **1c** (10^{-2} M) and variable concentrations of the electron donors tris-*p*-tolylamine (TTA) and 1,2,4,5-tetramethoxybenzene (TMB) (10^{-5} – 10^{-4} M). In the presence of TTA, the decay at 540 nm occurred with the same pseudo-first-order rate constant as the grow-in at 670 nm, the absorbance maximum of the TTA^{•+}.¹⁶ The slopes of the plots of the rate constants for grow-in of the TTA^{•+} at 670 nm and the TMB^{•+} at 460 nm¹⁶ (plots not shown) gave the bimolecular rate constants 1.5×10^{10} and 8×10^9 M⁻¹ s⁻¹, respectively, consistent with oxidation of the donors by **1c**⁺ to

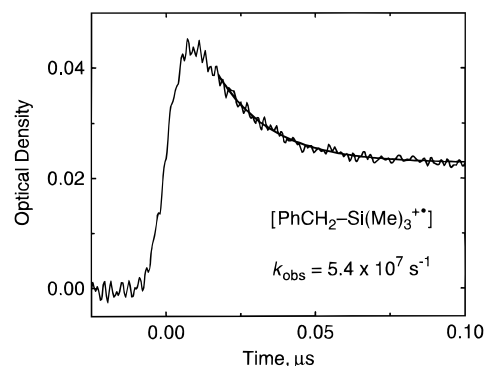


Figure 3. Time-resolved absorption decay observed at 550 nm for excitation of *N*-methylquinolinium (NMQ) hexafluorophosphate with toluene as the cosensitizer in the presence of benzyltrimethylsilane (**1a**) in argon-purged dichloromethane solution. The decay is due to the silane cation radical. Under these conditions the concentration of the *N*-methylquinolyl radical (NMQ[•]) is essentially constant with time.

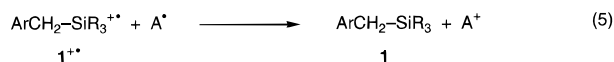
give the donor cation radicals (eq 3). These experiments, together with the observed reactivity toward added nucleophiles (see below), confirm that the 540 nm transient is the cation radical of benzyltriisopropylsilane.

NMQ hexafluorophosphate/toluene-sensitized oxidation of benzyltrimethylsilane (**1a**) in dichloromethane solution also resulted in transient absorptions with a maximum at ca. 540 nm. In this case, no long-lived absorptions were observed in oxygen-purged solutions. In argon-purged solutions, a short-lived absorption was observed at 550 nm with a lifetime of ca. 20 ns, followed by a longer-lived absorption which decayed on a microsecond time scale (Figure 3). In the absence of oxygen, the decay of NMQ[•] is relatively slow, and the fast decay is thus presumably due to a rapid, pseudo-first-order reaction of the cation radical of **1a**. As with the benzyltriisopropylsilane, experiments at different wavelengths showed that the absorption of **1a**⁺ overlapped extensively with that of NMQ[•], since the short-lived decay was always accompanied by the longer-lived decay. From these experiments, however, it was clear that the absorption maximum of **1a**⁺ was approximately 530 nm.

Because of the short lifetime in this case, confirmation that the fast decaying transient was **1a**⁺ could not be obtained using electron transfer reactions such as those described above using TMB and TTA. Instead, a different approach was taken—generation of **1a**⁺ from an independent source. Excitation of ground state charge transfer (CT) complexes leads to the formation of ion radical pairs.¹⁷ Benzyltrimethylsilane and 1,2,4,5-tetracyanobenzene (TCB) form a CT complex in chloroform, characterized by a broad absorption band with a maximum at ca. 360 nm. Excitation of this complex with a picosecond laser pulse at 355 nm yields a transient absorption spectrum with two maxima, as shown in Figure 4. The maximum at 465 nm is consistent with that observed previously for TCB^{•-}.¹⁶ The band with the maximum at ca. 530 nm is not due to TCB^{•-} and is therefore most reasonably assigned to the benzyltrimethylsilane cation radical. Under these conditions, both absorption bands decay with the same rate constant (9×10^9 s⁻¹), presumably via return electron transfer to regenerate the ground state CT complex. The similarity of the absorbances observed in this experiment and in the NMQ-sensitized oxidation of **1a** to the transient absorption spectrum assigned to **1c**⁺

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to the propensity of the solvent toward strong hydrogen-bonding interactions. These results provided further support for an S_N2 mechanism in the other solvents studied.

Thus, $1a^{+\bullet}$ appears to be very susceptible to nucleophilic attack by water and other nucleophiles, as confirmed by measurements of bimolecular rate constants (see the next section). It is obviously difficult to measure the rate constant for unimolecular (S_N1) reaction for this species, since the cleavage seems to be controlled by small concentrations of impurities such as water. The upper limit for the S_N1 reaction is presumably given by the slowest rate of decay observed in the presence of the lowest concentrations of adventitious nucleophilic impurities. For $1a^{+\bullet}$, this would be $7.1 \times 10^5 \text{ s}^{-1}$, measured in hexafluoro-2-propanol (see above). However, a better estimate may be obtained from the reactions of the triisopropyl derivative $1c^{+\bullet}$. The cation radical of this compound is less susceptible to nucleophilic attack due to steric hindrance at silicon, and thus the rate of unimolecular cleavage should be better defined. The lifetime of the triisopropyl derivative is longest in hexafluoro-2-propanol. Under these conditions, the first-order decay rate is estimated to be *less* than ca. 10^4 s^{-1} , which is thus the upper limit for the rate constant of the S_N1 reaction. Obviously this is much less than the rate constant for decay of benzyltrimethylsilane cation radical under all of the conditions investigated, which demonstrates that the reactions of this cation radical must undoubtedly be due to nucleophile-assisted cleavage by the solvent or a nucleophilic impurity.

C. Reactivity of Benzyltrialkylsilane Cation Radicals.

Absolute rate constants for the second-order reaction of silane cation radicals with nucleophiles are readily obtained as the slopes of plots of the pseudo-first-order rate constants (k_{obs}) for decay of the cation radical vs nucleophile concentration. Values for these rate constants have been reported previously by us for (4-methoxybenzyl)trialkylsilane cation radicals.^{3a} Having now identified the more reactive benzyltrialkylsilane cation radicals and determined the conditions under which their lifetimes were long enough to study reactions with nucleophiles, we were in a position to broaden the scope of these studies. A typical experiment is illustrated in Figure 5, where the rate constant for pseudo-first-order decay of benzyltrimethylsilane cation radical is plotted vs acetonitrile concentration. The experiment was performed using the TCB/toluene sensitization system in dried dichloromethane, to ensure a sufficiently long lifetime for the cation radical in the absence of added acetonitrile. The experiment illustrated in Figure 5 quantitatively demonstrates the high reactivity of acetonitrile as a nucleophile for the cation radical of $1a$ ($k_{\text{Nu}} = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

Several of the factors that influence the rate constants for the reaction of the cation radicals with nucleophiles were investigated. These included (1) substituents on the phenyl ring that alter the oxidation potential of the silane, (2) alkyl substituents on silicon that have variable steric restrictions, (3) the chemical nature and steric influences of the nucleophiles, and (4) solvent properties.

Rate constants were measured for the reaction of methanol as a nucleophile with silanes $1a\text{--}e$ in hexafluoro-2-propanol and dichloromethane (Table 1).²⁰ The second-order rate

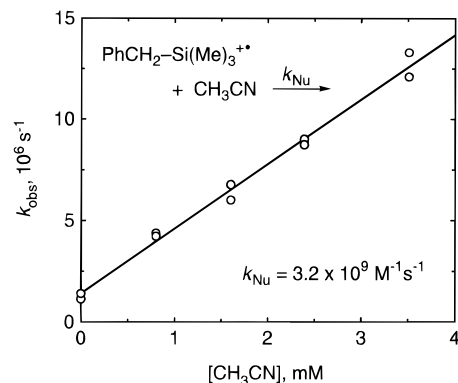


Figure 5. Plot of the pseudo-first-order rate constant for decay of benzyltrimethylsilane cation radical ($1a^{+\bullet}$) formed using the 1,2,4,5-tetracyanobenzene/toluene sensitization system in dried dichloromethane (see text), as a function of the concentration of added acetonitrile.

Table 1. Substituent and Solvent Effects on the Second-Order Rate Constants (k_{Nu}) for the Reaction of Benzylsilane Cation Radicals with Methanol as a Nucleophile^a

	[4-X-C ₆ H ₄ CH ₂ -SiR ₃] ⁺		k_{Nu} (M ⁻¹ s ⁻¹)	
	X	R	HFIP	DCM
1a	H	CH ₃	1.3×10^7	2.9×10^9
1d	CH ₃	CH ₃	4.3×10^6	5.7×10^8
1e	OCH ₃	CH ₃	$< 2 \times 10^5$	1.5×10^7
1b	H	CH ₂ CH ₃	2.4×10^6	6.1×10^8
1c	H	CH(CH ₃) ₂	$< 2 \times 10^5$	8.9×10^5

^a Rate constants measured at room temperature in hexafluoro-2-propanol (HFIP) and dichloromethane (DCM).

constants for reaction of methanol with the cation radicals decrease with increasing electron-donating ability of substituents on the phenyl ring. The rate constants decrease by a factor of 3–5 for the 4-methyl derivative **1d**, compared to the unsubstituted analogue **1a**, and by approximately 2 orders of magnitude for the lowest oxidation potential compound, the 4-methoxy derivative **1e**. This trend is expected on thermokinetic grounds. Using a thermodynamic cycle, it can easily be shown that the C–Si bond dissociation energy in the cation radical increases with decreasing oxidation potential of the silane (i.e., in the order $1a < 1d < 1e$).²¹ In addition, localization of the positive charge on the aryl ring will presumably increase with increasing electron-donating ability of the substituent, making it more difficult to transfer positive charge out of the aryl group to silicon and the nucleophile, thus increasing the barrier to reaction.

As expected for an S_N2 mechanism, the rate constants are very sensitive to the steric nature of the alkyl substituents at silicon. As shown in Table 1, changing the alkyl group, R, from methyl to isopropyl causes the rate constant to decrease by ca. 3 orders of magnitude. Increasing the steric crowding on the nucleophile also has the effect of decreasing the rate constant (Table 2). In dichloromethane and acetonitrile as solvents, the rate constants for the reaction with 2-propanol are ca. 20% of those for reaction with methanol. The rate constants with *tert*-butyl alcohol are only 5–7% of those for methanol (Table 2). A smaller difference in reaction rates is observed in hexafluoro-2-propanol, which may reflect the unique hydrogen-bonding properties of this solvent (see further below).

It is interesting to note that the reactivity of acetonitrile as a nucleophile relative to that of methanol seems to vary signifi-

(20) When methanol was used as a nucleophile in hexafluoro-2-propanol, some plots of the pseudo-first-order decay constants of the silane cation radicals as a function of methanol concentration showed upward curvature at high methanol concentrations ($\geq 0.3 \text{ M}$). The rate constants reported here are all from plots with alcohol concentrations low enough to ensure linearity.

(21) The bond dissociation energy of the cation radical (BDE_{CR}) is given by the following equation: $BDE_{\text{CR}} = BDE_{\text{N}} - IP_{\text{N}} + IP_{\text{R}^{\bullet}}$, where BDE_{N} is the bond dissociation energy of the neutral compound, IP_{N} is the ionization potential of the neutral compound, and $IP_{\text{R}^{\bullet}}$ is the lower ionization potential of the two radicals formed upon bond homolysis of the neutral compound, in this case $\bullet\text{SiR}_3$ (ref 3a).

Table 2. Comparison between the Second-Order Rate Constants (k_{Nu}) for the Reaction of Benzylsilane Cation Radicals with Methanol, 2-Propanol, and *tert*-Butyl Alcohol as Nucleophiles

[4-X-C ₆ H ₄ CH ₂ -SiR ₃] ⁺						
	X	R	solvent ^a	Nu	k_{Nu} (M ⁻¹ s ⁻¹)	(k_{Nu}) _{rel} ^b
1a	H	CH ₃	HFIP	MeOH	1.3 × 10 ⁷	(1.0)
				<i>i</i> -PrOH	6.5 × 10 ⁶	0.5
				<i>t</i> -BuOH	2.5 × 10 ⁶	0.19
1e	OCH ₃	CH ₃	DCM	MeOH	1.5 × 10 ⁷	(1.0)
				<i>i</i> -PrOH	2.9 × 10 ⁶	0.19
				<i>t</i> -BuOH	7.3 × 10 ⁵	0.049
1e	OCH ₃	CH ₃	AN	MeOH	5.5 × 10 ⁶	(1.0)
				<i>i</i> -PrOH	9.7 × 10 ⁵	0.18
				<i>t</i> -BuOH	4.1 × 10 ⁵	0.074

^a The solvents are hexafluoro-2-propanol (HFIP), dichloromethane (DCM), and acetonitrile (AN). ^b Relative rate constants to that with methanol as a nucleophile.

Table 3. Comparison between the Second-Order Rate Constants (k_{Nu}) for the Reaction of Benzylsilane Cation Radicals with Methanol and with Acetonitrile as Nucleophiles

[4-X-C ₆ H ₄ CH ₂ -SiR ₃] ⁺						
X	R	solvent	k_{Nu} (M ⁻¹ s ⁻¹)		R^a	
			Nu = CH ₃ OH	Nu = CH ₃ CN		
1a	H	CH ₃	HFIP	1.3 × 10 ⁷	3.6 × 10 ⁷	0.36
1a	H	CH ₃	DCM	2.9 × 10 ⁹	3.2 × 10 ⁹	0.90
1b	H	CH ₂ CH ₃	DCM	6.1 × 10 ⁸	6.4 × 10 ⁸	0.95
1c	H	CH(CH ₃) ₂	DCM	8.9 × 10 ⁵	6.4 × 10 ⁵	1.4
1e	OCH ₃	CH ₃	DCM	1.5 × 10 ⁷	5.5 × 10 ⁵	27
1e	OCH ₃	CH ₃	AN	5.5 × 10 ⁶	(1.2 × 10 ⁵) ^b	46

^a Ratio of the rate constant (k_{Nu}) for the reaction with methanol to that with acetonitrile as nucleophile. ^b Estimated from the measured decay rate^{3a} of 2.3 × 10⁶ s⁻¹ in neat acetonitrile, divided by 19, the molarity of acetonitrile.

cantly. As shown in Table 3, the benzylsilane cation radicals in dichloromethane exhibit similar rate constants in their reactions with either of these nucleophiles, whereas the 4-methoxy derivative is 30–40 times more reactive toward methanol than toward acetonitrile. The reason for this difference is not clear. It may be a consequence of the different charge densities on silicon in the cation radicals of the benzyl and the 4-methoxybenzyl derivatives. Alternatively, the reactivity difference for the 4-methoxy compound **1e** may simply reflect the fact that methanol is a better nucleophile toward benzylsilane cation radicals than acetonitrile. If this is true, then the benzyltrimethylsilane cation radical (**1a**⁺) may not distinguish between the two nucleophiles simply because the rate constants are only ca. 5 times smaller than the diffusion-controlled limit. The rate constants for reaction with the triisopropyl derivative **1c**⁺ are smaller than those for **1a**⁺ because of steric interactions, which may be similar for both nucleophiles. In HFIP, acetonitrile actually reacts faster than methanol with the benzyltrimethylsilane cation radical, presumably because of differences in hydrogen-bonding interactions between the nucleophiles and the solvent. The influence of HFIP as the solvent on the absolute values of the rate constants compared to dichloromethane is dramatic. The rate constants with methanol as the nucleophile decrease by ca. 2 orders of magnitude in HFIP, as indicated in Table 1. A similar effect is also observed with acetonitrile as a nucleophile, as shown for the reactions of **1a**⁺ shown in Table 3.

The bimolecular rate constants for the cation radicals studied here with methanol and acetonitrile are sufficiently high that for reactions performed in these solvents, reaction with the solvent would always be much faster than the limiting rate for the S_N1 reaction of <10⁴ s⁻¹. For **1a**, the rate constant for reaction of the cation radical with water as the nucleophile was

measured in HFIP and found to be 2 × 10⁷ M⁻¹ s⁻¹ (not included in the tables). This is very similar to the rate constant for methanol under the same conditions (Table 1). The lifetime of **1a**⁺ in dichloromethane for which no particular drying procedure was applied was ca. 20 ns. If the rate constant for reaction of water is similar to that of methanol in this solvent (2.9 × 10⁹ M⁻¹ s⁻¹, Table 1), then a water content of only 0.02% would account for the short lifetime of the benzyltrimethylsilane cation radical. Clearly, with a cation radical as reactive as **1a**⁺, unusual care has to be taken to minimize the effects of adventitious nucleophiles. For this reason the S_N2 process appears to dominate the cleavage reactivity of the benzyltrialkylsilanes studied here.

III. Concluding Remarks

The absolute rate constants for bimolecular nucleophile-assisted (S_N2) C–Si bond cleavage of benzyltrimethylsilane cation radical, with acetonitrile and methanol as nucleophiles in non-hydrogen-bonding solvents, are ca. 3 × 10⁹ M⁻¹ s⁻¹. The estimated upper limit for unimolecular (S_N1) C–Si bond cleavage for this cation radical is estimated to be <10⁴ s⁻¹. These data indicate that unless unusual precautions are taken to exclude adventitious nucleophiles, such as traces of water, to concentrations well below 10⁻⁵ M, the S_N2 mechanism will be the dominant reaction pathway for the benzyltrimethylsilane cation radical.

The large values for the second-order rate constants measured here clearly demonstrate the viability of the S_N2 mechanism. The generality of the mechanism for cation radicals other than those derived from silanes has yet to be fully established; however, it would seem reasonable to consider the possibility of nucleophilic assistance in the cleavage reactions of related cation radicals, such as those of stannanes and germanes.^{2e,3c,7}

IV. Experimental Section

Materials. Acetonitrile (Fisher) was distilled under nitrogen from CaH₂. Dichloromethane (Aldrich) and toluene (Baker Photrex) were used as received. Hexafluoro-2-propanol (Acros) was successively distilled from sodium bicarbonate and activated molecular sieves (3 Å). In some cases, dichloromethane was distilled under nitrogen from CaH₂ prior to use, although identical results were obtained with spectral grade solvent. Spectral grade methanol, 2-propanol, and *tert*-butyl alcohol were obtained from commercial sources and used as received. 1,2,4,5-Tetracyanobenzene (TCB) (TCI America) was recrystallized from chloroform. 1,2,4,5-Tetramethoxybenzene (TMB) was generously provided by Kodak. Tris-*p*-tolylamine (TTA) was prepared by a literature procedure.²² Benzyltrimethylsilane (**1a**) (Aldrich) was distilled prior to use. Benzyltriethylsilane (**1b**), benzyltriisopropylsilane (**1c**), and (4-methylbenzyl)trimethylsilane (**1d**) were prepared by reaction of benzylmagnesium chloride with the appropriate chlorotrialkylsilane and purified by distillation.²³ (4-Methoxybenzyl)trimethylsilane (**1e**) was prepared in similar fashion from the corresponding benzyl chloride using activated magnesium.²⁴

Physical Methods. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 or GE QE-300 NMR spectrometer. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the solvent as an internal standard (CHD₂CN (¹H) 1.93; CHCl₃ (¹H) 7.24, (¹³C) 77.0). UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. Detailed descriptions of the nanosecond and picosecond transient absorption apparatus are given elsewhere.^{25,26}

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Transient Absorption Experiments. Experiments with *N*-methylquinolinium (NMQ) as the sensitizer were performed in either dichloromethane, acetonitrile, or hexafluoro-2-propanol solutions containing NMQ (OD \approx 0.5 at 345 nm), toluene (1 M), and the appropriate silane (0.02 M). In experiments where the influence of adventitious water was to be minimized, the solutions were dried by storage over 3 Å activated molecular sieves for 2 h. Samples in 1 cm² cuvettes were irradiated at 345 nm, except when TMB was added, in which case the excitation wavelength was 360 nm.

Irradiation of the TCB/benzyltrimethylsilane charge transfer complex at 355 nm was performed with a TCB-saturated chloroform-*d* solution containing benzyltrimethylsilane (1.33 M). The CT complex had a broad absorption with $\lambda_{\max} \approx$ 360 nm.

Experiments with the TCB/toluene charge transfer complex were carried out in dichloromethane solutions containing TCB (1.0 mM), toluene (1.1 M), and silane (0.026 M).

Preparation of *N*-Methylquinolinium (NMQ) Salts. All manipulations were performed in low-light conditions. *N*-Methylquinolinium tetrafluoroborate was prepared by a literature procedure.²⁷ *N*-Methylquinolinium hexafluorophosphate was prepared by addition of *N*-methylquinolinium iodide²⁸ (10.6 g, 39 mmol) in water (200 mL) to a solution of potassium hexafluorophosphate (7.6 g, 41 mmol) in water

(200 mL). A white precipitate formed which was collected, rinsed with cold water, and dried *in vacuo*. The crude product was recrystallized twice from water to give 5.3 g (47%) of colorless crystals: mp 218–219 °C. ¹H NMR (CD₃CN): δ 9.08 (d, *J* = 9 Hz, 1 H), 9.04 (d, *J* = 6 Hz, 1 H), 8.40–8.20 (m, 3 H), 8.05–7.95 (m, 2 H), 4.55 (s, 3 H). ¹³C NMR (DMSO-*d*₆): δ 150.1, 147.0, 138.3, 135.4, 130.2, 129.8, 129.1, 121.9, 119.0, 45.2. Anal. Calcd for C₁₀H₁₀N₁P₁F₆: C, 41.54; H, 3.49; N, 4.84. Found: C, 41.84; H, 3.48; N, 4.87.

N-Methylquinolinium hexafluoroantimonate was prepared by addition of *N*-methylquinolinium iodide (5.10 g, 18.8 mmol) in dry acetonitrile (120 mL) to a solution of silver hexafluoroantimonate (6.49 g, 18.9 mmol) in dry acetonitrile (25 mL). Filtration followed by removal of solvent *in vacuo* gave a white solid which was recrystallized from dichloromethane to give 2.1 g (29%) of white crystals: mp 244–245 °C. The ¹H and ¹³C NMR spectra were identical to that of the hexafluorophosphate salt. Anal. Calcd for C₁₀H₁₀N₁Sb₁F₆: C, 31.61; H, 2.65; N, 3.69. Found: C, 31.51; H, 2.68; N, 3.69.

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