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INTRAMOLECULAR NUCLEOPHILE-ASSISTED CLEAVAGE OF ORGANOSILANE CATION RADICALS

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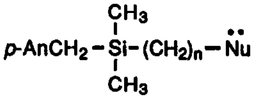
Summary: *Organosilane cation radicals which have tethered nucleophiles are found to undergo rapid intramolecular nucleophilic substitution in both high and low polarity solvents. This reaction competes with both separation and return electron transfer within the primary ion radical pair generated by photoinduced bimolecular electron transfer. These results demonstrate the ability to effect ion radical substitutions in low polarity solvents.*

The efficiency of photoinduced electron transfer reactions in solution is dependent on the fate of the primary ion radical pair, $A^{\cdot -}$ / $D^{\cdot +}$. Diffusional separation and rapid chemical reaction of $A^{\cdot -}$ and/or $D^{\cdot +}$ are two processes which can effectively compete with the energy wasting, chemically inefficient return electron transfer process.[1] Although separation of the ion radical pair occurs in highly polar solvents to yield free ions, in general it does not in low polarity solvents.[2c] Consequently, a general strategy to effect efficient chemistry in all solvents is to design rapid chemical reactions of the ion radical pair.

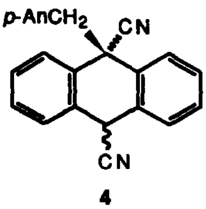
Recently, we reported on the rapid bond fragmentation reaction of organosilane cation radicals, a process which can compete with return electron transfer within the primary ion radical pair.[2] However, this fragmentation reaction requires nucleophilic assistance, for example, from a polar solvent molecule. Although the bimolecular nucleophilic rate constants are remarkably high, the nucleophile concentration must also be very high for the reaction to compete effectively with return electron transfer. To alleviate this restriction and to decrease the entropic constraints of the reaction, we have prepared several organosilanes which have nucleophiles tethered to the silicon by methylene chains of various lengths.[3] We now report on the generation of these organosilane cation radicals and their rate constants for nucleophilic substitution. The results indicate that they can undergo rapid reaction in both nucleophilic, high polarity solvents and non-nucleophilic, low polarity solvents.

The photosensitized oxidations of compounds 1-2 by 9,10-dicyanoanthracene (DCA) yield adduct 4 as a *cis/trans* mixture.[4]



$$p\text{-AnCH}_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-(CH_2)_n-\ddot{Nu}$$

Nu = OH	*Nu = OCH_3*
1a: n=3	**2a:** n=3
1b: n=4	**2b:** n=4
1c: n=5	**2c:** n=5



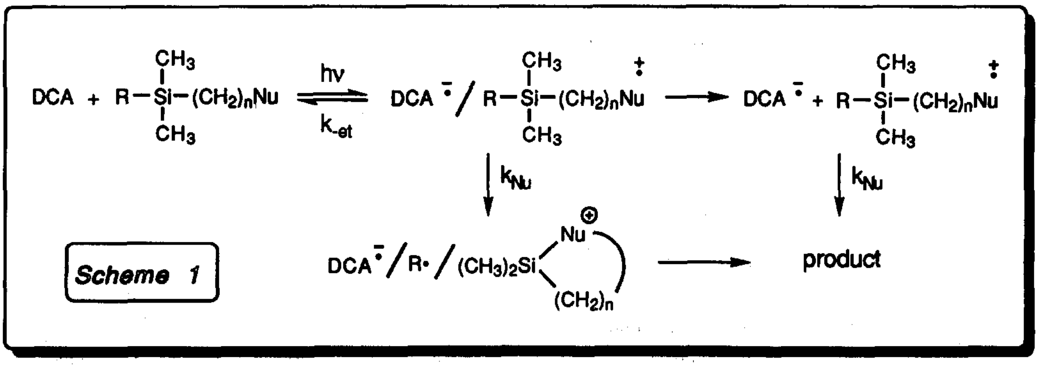
4

p-An = (p-CH_3O)C_6H_4-

The adduct is presumably formed as a result of intramolecular nucleophile-assisted cleavage of the carbon-silicon bond to yield the (*p*-methoxy)benzyl radical which, in turn, adds to the DCA anion radical, followed by protonation.[2a] The absolute quantum yields for the formation of adduct **4** from the nucleophile-linked compounds **1-2** and *p*-An$CH_2Si(CH_3)_3$, **3**, in various solvents are given in Table 1.[5]

Table 1	1a	1b	1c	2a	2b	2c	3
CH_3CN	0.034	0.016	0.011	0.035	0.016	0.014	0.013
CH_2Cl_2	0.023			0.048			0.0006
C_6H_5F	0.022			0.044			

In CH_3CN, the ion radical pair formed from photoinduced electron transfer from **3** to DCA undergoes only ion pair separation and return electron transfer.[2a] Nucleophilic displacement by the solvent on the cation radical $\mathbf{3}^{\ddagger}$ occurs following separation. The quantum yields for adduct formation from **1b-c** and **2b-c** are similar to that of **3**, which suggests that intramolecular nucleophilic displacement of the (*p*-methoxy)benzyl radical can not compete effectively with either ion pair separation or return electron transfer from within the ion pair, i.e. $k_{Nu} < k_{-et} + k_{sep}$ in Scheme 1. However, the quantum yields for **1a** and **2a** are significantly higher than for **3**. Assuming that the rates of return electron transfer and diffusional separation are similar in the series of tethered compounds, then intramolecular nucleophilic substitution must occur in competition with separation and return electron transfer for **1a** and **2a**.



Scheme 1

In CH_2Cl_2, the quantum yield for product formation from **3** is extremely low because both ion pair separation and intermolecular nucleophilic substitution are much slower than return electron transfer. However, the yields are much higher for **1a** and **2a** in CH_2Cl_2 and C_6H_5F, which suggests that intramolecular nucleophilic substitution, k_{Nu}, is competitive with return electron transfer, k_{-et}, in these solvents.

In order to evaluate the absolute rate constants for nucleophilic substitution, nanosecond transient absorption studies were performed.[6] The organosilanes **1-2** were photooxidized by electron transfer from biphenyl cation radical as previously described for **3**.[2] The absorption spectra observed following the oxidation of **1b,c** and **2b,c** are assigned to the respective organosilane cation radicals based on their similarity to that previously assigned to the cation radical **3**$^{+\bullet}$. The first order rates for disappearance of **1**$^{+\bullet}$-**2**$^{+\bullet}$ in various solvents were determined and are given in Table 2.

Table 2	k_{Nu} $(\times 10^6\ s^{-1})$						
	1a	**1b**	**1c**	**2a**	**2b**	**2c**	**3**
CH_3CN	> 50	2.7	1.9	> 50	9.0	2.0	2.3
CH_2Cl_2	> 50	23.0	< 0.3	> 50	15.0	< 0.1	---

We attribute the disappearance of the organosilane cation radicals to nucleophilic substitution at silicon. In CH_3CN, the rate of nucleophilic substitution, k_{Nu}, for **1b**$^{+\bullet}$,**1c**$^{+\bullet}$, and **2c**$^{+\bullet}$ are within experimental error of that for **3**. This suggests that the solvent acts as the nucleophile rather than the tethered alcohol. However, k_{Nu} for **2b**$^{+\bullet}$ is significantly faster than for **3**$^{+\bullet}$, indicating intramolecular nucleophilic participation from the tethered methoxy group. Under the photooxidation conditions employed to generate and observe the cation radicals from **1b,c** and **2b,c**, no transient absorptions attributable to **1a**$^{+\bullet}$ or **2a**$^{+\bullet}$ could be detected, presumably due to rapid intramolecular substitution. This suggests that the lifetimes of **1a**$^{+\bullet}$ and **2a**$^{+\bullet}$ are too short to be detected under our experimental conditions, i.e. < 20 ns.

In CH_2Cl_2, **3**$^{+\bullet}$ is long-lived and decays predominantly by second order return electron transfer with DCA$^{-\bullet}$. The decays of **1c**$^{+\bullet}$ and **2c**$^{+\bullet}$ are concentration dependent, which suggests that they undergo a mixture of intra- and intermolecular nucleophilic substitution reactions.[7] However, only intramolecular substitution occurs for **1b**$^{+\bullet}$ and **2b**$^{+\bullet}$ as their decays are first order and concentration independent. No transient absorption is observed for either **1a**$^{+\bullet}$ and **2a**$^{+\bullet}$, which suggests that their lifetimes are < 20 ns.[8]

Several interesting aspects of this S_N2 reaction are illustrated by these rate constant data. First, k_{Nu} for each series of compounds decreases from n=3 to n=4 to n=5, independent of nucleophile and solvent. Previous experiments have found the same ring size effect for the rates of intramolecular nucleophilic displacement at silicon in neutral substrates.[9] Second, k_{Nu} for **1b**$^{+\bullet}$ and **2b**$^{+\bullet}$ in CH_2Cl_2 are greater than in CH_3CN. This is consistent with a mechanism in which charge is dispersed in the transition state; increased solvent polarity resulting in lower S_N2 rate constants.[2b] Third, although the k_{Nu} for **1b**$^{+\bullet}$ and **2b**$^{+\bullet}$ are similar in CH_2Cl_2, $k_{Nu}(\mathbf{2b}^{+\bullet}) > k_{Nu}(\mathbf{1b}^{+\bullet})$ in CH_3CN, which implies that the methoxy group is a better nucleophile than a hydroxy group in CH_3CN but not in CH_2Cl_2. Fourth, the observed rate constants support the quantum yield results. In CH_3CN, assuming $k_{sep} = 5 \times 10^8\ s^{-1}$,[1a] then only **1a**$^{+\bullet}$ and **2a**$^{+\bullet}$ will undergo competitive intramolecular nucleophilic displacement within the primary ion radical pair. The other cation radicals react either intra- or intermolecularly after separation has occurred.

In conclusion, we have prepared several nucleophile-tethered organosilanes in an effort to increase the rate at which their cation radicals undergo nucleophilic substitution in non-nucleophilic solvents. When n=3, nucleophilic substitution is rapid within the primary ion radical pair and competes with both ion pair separation and return electron transfer in solvents of high and moderate polarity. Studies are in progress to design other fast ion radical reactions which can occur efficiently under photoinduced electron transfer conditions.

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1. For reviews see: (a) Mattes, S. L.; Farid, S. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (c) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (d) Fox, M. A. In "Advances in Photochemistry"; Volman, D. H.; Gollnick, K.; Hammond, G. S., Eds.; Wiley: New York, 1986, Vol. 13, p 237.
2. (a) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8973. (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 151. (c) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 3601.
3. Similar experiments have recently been described for the cleavage reactions of polysilane cation radicals, although no relative quantum yield or rate constant data were reported. See, Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327.
4. The compounds **1a-c** and **2a-c** were synthesized via H_2PtCl_6 coupling of 4-methoxybenzyldimethylsilane and the appropriately tethered alkoxy or hydroxy (protected as acetate) olefins. These compounds were satisfactorily characterized by ^1H NMR. ^1H NMR of the reaction mixture from oxidation of **1-2** showed *cis* and *trans* **4**. Compound **4** was characterized by its oxidation product, 10-(4-methoxybenzyl)-10-cyano-9,10-dihydro-9-oxoanthracene, **5**.
5. Quantum yields for the formation of anthrone **5** were determined by *trans*-stilbene/9,10-phenanthrenequinone actinometry (see Bohning, J. J.; Weiss, K. *J. Am. Chem. Soc.* **1966**, *88*, 2893). The argon-purged silane samples were irradiated at 405 nm, then heated with added O_2 and *N,N*-diisopropylethylamine. The resulting anthrone **5** was quantified by GC analysis.
6. For a description of the time-resolved spectroscopy apparatus, see Gould, I. R.; Ege, D., Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
7. The rate constants for **1c**$^{+\bullet}$ and **2c**$^{+\bullet}$ in CH_2Cl_2 are from extrapolation of the first-order decay rate constants to zero concentration of **1c** and **2c**.
8. Picosecond transient absorption studies indicate that the rates of decay of the DCA$^{-\bullet}$ / **3**$^{+\bullet}$ ion pairs (λ_{mon} = 705, 615, 500 nm) formed from the oxidation of **3** are 1.1×10^9 and 2.7×10^9 s^{-1} in C_6H_5F and CH_2Cl_2, respectively. Assuming these decays are due to return electron transfer and these rates are similar for the tethered silanes **1a** and **2a** in these solvents, then using the measured quantum yields, the calculated rate constants for intramolecular nucleophilic substitution, k_{Nu}, are 6.4×10^7 and 1.4×10^8 s^{-1} in CH_2Cl_2, and 2.5×10^7 and 5.1×10^7 s^{-1} in C_6H_5F for **1a** and **2a**. These results are in reasonable agreement with the nanosecond absorption experiments which indicate k_{Nu} for **1a** and **2a** is $> 5 \times 10^7$ s^{-1}. Full details will be published later.
9. Wittenberg, P.; Gilman, H. *J. Am. Chem. Soc.* **1958**, *80*, 2677.

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