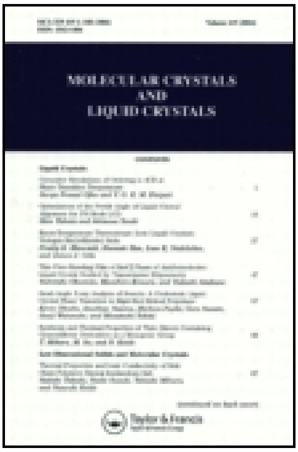


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Photooxidative Cleavage of Organosilanes

J. P. Dinnocenzo [a] [b], S. Farid [a] [c], J. L. Goodman [a] [b], I. R. Gould [a] [c] & W. P. Todd [a] [b]

[a] Center for Photoinduced Charge Transfer, University of Rochester, Hutchison Hall, Rochester, NY, 14627

[b] Department of Chemistry, University of Rochester, Rochester, NY, 14627

[c] Corporate Research Laboratories, Eastman Kodak Company, Rochester, NY, 14650-2109

Version of record first published: 04 Oct 2006.

To cite this article: J. P. Dinnocenzo , S. Farid , J. L. Goodman , I. R. Gould & W. P. Todd (1991): Photooxidative Cleavage of Organosilanes, Molecular Crystals and Liquid Crystals, 194:1, 151-157

To link to this article: http://dx.doi.org/10.1080/00268949108041160

Mol. Cryst. Liq. Cryst., 1991, vol. 194, pp. 151–157
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PHOTOOXIDATIVE CLEAVAGE OF ORGANOSILANES

J. P. DINNOCENZO,† S. FARID,‡ J. L. GOODMAN,† I. R. GOULD,‡ AND W. P. TODD†
Center for Photoinduced Charge Transfer, University of Rochester, Hutchison Hall, Rochester, NY 14627

† Department of Chemistry, University of Rochester, Rochester, NY 14627
‡ Corporate Research Laboratories, Eastman Kodak Company, Rochester, NY 14650-2109

Abstract Avoiding energy wasting return electron transfer reactions remains a central challenge in the design of high efficiency photoinduced electron transfer processes. One strategy for achieving this goal is to utilize compounds which as a result of electron transfer undergo rapid and irreversible chemical reaction in competion with the return electron process. Organosilanes represent a promising class of compounds that may fulfill this requirement. We have found that some organosilanes undergo rapid carbon-silicon bond cleavage when oxidized to their radical cations in photoinduced electron transfer reactions. Interestingly, these radical cation cleavage reactions occur by a rare nucleophile-assisted mechanism. We have investigated the reactivity of different classes of nucleophiles, and have determined the activation parameters for several of these reactions.

Keywords: Organosilane, photooxidative cleavage, photoinduced electron transfer, nucleophile, activation energy

INTRODUCTION

Some applications of photoinduced electron transfer processes require high chemical stability of the species formed when the electron is transferred, for example in electrophotography and in photovoltaic devices, in which no net chemical transformation is usually an essential condition. Other applications, however, are based upon the chemical reactions of the charge separated species, for example in many imaging systems in which photoinduced radical ion formation results in polymerization reactions. Studies which explore new chemical reactions based on photoinduced electron transfer procceses are, therefore, of general interest.[1] An additional objective of such investigations is an understanding of the factors which control the efficiencies of such reactions. High efficiency reactions can be achieved if useful processes can compete favorably with the energy wasting return electron transfer process within the initially formed charge separated species (the geminate radical-ion pair).[2] Therefore for an efficient reaction, either the rate of the return electron transfer process must be low, or the rate of chemical reaction of the radical ions must be high. Previous studies on the return electron transfer process have clearly defined the factors controlling the rates of these reactions.[2] In this paper we describe work directed toward an understanding of the rates of chemical reaction of a class of potentially useful radical cations.

Of the several known radical cation reactions,[1] e.g., rearrangements, additions, oxygenations, etc., fragmentation reactions are currently attracting considerable interest. In particular, C-C[3] and C-Si[4] bond cleavage reactions have attracted attention as possibly efficient and useful processes. We reported recently that the fragmentation of organosilane radical cations occurs via a nucleophile-assisted step which seems to significantly lower the activation energy for fragmentation, and thus leads in an increase in the rate constant for cleavage.[5] We now report on the reactivity of different classes of nucleophiles in assisting the C-Si bond cleavage, and on the activation parameters for these reactions.

RESULTS AND DISCUSSION

In the current work we studied the fragmentation of the radical cation of methoxybenzyltrimethylsilane (S), which was generated via a secondary, exothermic electron transfer to

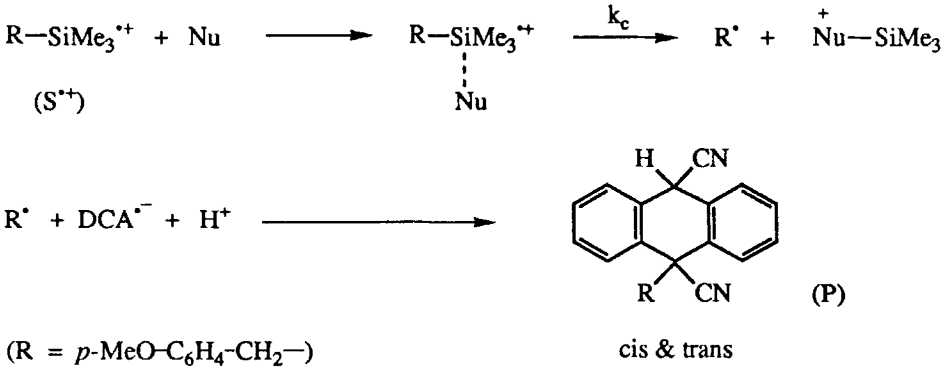
$$p\text{-MeO–}C_6H_4\text{–}CH_2\text{–}SiMe_3 \qquad (S)$$

biphenyl (BP) radical cation. The latter was formed photochemically via an electron transfer reaction with the first singlet excited state of 9,10-dicyanoanthracene (DCA) in

$$^1DCA^* + BP \longrightarrow DCA^{\bullet -} + BP^{\bullet +}$$

$$BP^{\bullet +} + S \longrightarrow BP + S^{\bullet +}$$

acetonitrile. This route was chosen since the energetics of this photochemical process result in the formation of free radical ions in acetonitrile ($DCA^{\bullet -}$ + $BP^{\bullet +}$) with a high quantum yield ($\Phi = 0.75$).[2] The rate of cleavage of $S^{\bullet +}$ in the presence of added nucleophiles (k_c) was determined by measuring the rate of decay of the absorbance of $S^{\bullet +}$, monitored at 500 nm (λ_{max} of $S^{\bullet +}$), in a laser flash photolysis experiment (410 nm, 15 ns, 5 mJ).[5] In all cases we confirmed that the observed decay of $S^{\bullet +}$ is indeed due to fragmentation by performing analogous steady state photolysis experiments which demonstrated that the quantum yield of the cleavage product is not diminished in the presence of the added nucleophiles. Cleavage of $S^{\bullet +}$ leads to the methoxybenzyl radical ($R^{\bullet}$), which adds to $DCA^{\bullet -}$, and upon protonation yields the addition product (P).



$$R{-}SiMe_3^{\bullet +} + Nu \longrightarrow \underset{\vdots \atop Nu}{R{-}SiMe_3^{\bullet +}} \xrightarrow{k_c} R^{\bullet} + \overset{+}{Nu}{-}SiMe_3$$

($S^{\bullet +}$)

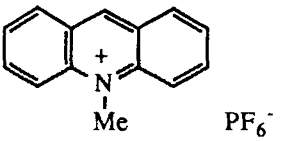
$R^{\bullet} + DCA^{\bullet -} + H^+ \longrightarrow$ (P)

cis & trans

($R = p\text{-}MeO\text{-}C_6H_4\text{-}CH_2\text{—}$)

We postulated previously that acetonitrile, which is the solvent used in these experiments, can act as a nucleophile and assist the cleavage reaction even in the absence of other additives.[5] Support for this idea was obtained from the observation that the lifetime of $S^{\bullet +}$ in acetonitrile increases upon replacement of the methyl groups in S by ethyl, and more dramatically by *iso*-propyl groups, i.e. with increased steric hinderence at the Si atom. Since acetonitrile was used as a solvent in these experiments, the actual bimolecular rate constant (k_c) could not be accurately determined in this case. We sought, therefore, a non nucleophilic solvent to carry out such reactions in which the concentration of acetonitrile could be varied.

Non nucleophilic solvents are usually less polar than acetonitrile. The quantum yields for free radical ion formation, however, are usually quite low in less polar solvents due to the increase in columbic attraction in the geminate radical-ion pair, and the decreased stabilization of the free radical ions in the less polar medium, which suggests that the transient absorption experiments might not be possible under these conditions. If, however, we use a cationic excited state acceptor, N-methylacridinium (MA^+), in place of the DCA, there is no columbic attraction in the initially formed geminate pair, since a neutral radical and a radical cation are formed in this case. Indeed, reaction of photoexcited MA^+ with BP in methylene chloride results in the formation of free $BP^{\bullet+}$ with a very high quantum yield. Secondary electron transfer as described above between $BP^{\bullet+}$ and S yields $S^{\bullet+}$ with high efficiency. In methylene chloride the radical cation $S^{\bullet+}$ is considerably longer lived than in acetonitrile. Indeed, the decay of $S^{\bullet+}$ in this solvent occurs mostly through a second order process, namely the diffusive recombination with $MA^\bullet$. In the presence of added nucleophiles, however, the decay of the silane radical cation is purely first order.



(MA^+)

$$MA^{+*} + BP \xrightarrow[(\Phi \approx 1)]{CH_2Cl_2} MA^\bullet + BP^{\bullet+}$$

From measurements of the increased rate of decay of $S^{\bullet+}$ in methylene chloride, as a

Table I Nucleophile-Induced Cleavage Rate Constants of the Silane Radical Cation ($S^{\bullet+}$) in Acetonitrile and in Methylene Chloride

Nucleophile (Nu)	$(k_c)_{acetonitrile}$ (10^6 $M^{-1}s^{-1}$)	$(k_c)_{methylene\ chloride}$ (10^6 $M^{-1}s^{-1}$)
methanol	5.5	15.3
iso-propanol	0.97	2.9
tert-butanol	0.41[a]	0.73
tetrahydrofuran	----	4.1
acetonitrile	(0.12)[b]	0.55
4-methylpyridine	12.5	----
pyridine	8.8	----
3-chloropyridine	1.9	----
2,6-dimethylpyridine	5.1	----

[a] This value is probably less accurate, since the change in decay rate in the presence and absence of *tert*-butanol is relatively small. [b] This value is an estimate obtained from the measured decay rate of $S^{\bullet+}$ in acetonitrile of 2.3×10^6 s^{-1}, divided by 19, the molarity of acetonitrile.

function of increasing concentration of added acetonitrile, a value for k_c of 5.5×10^5 $M^{-1}s^{-1}$ was obtained. The corresponding rate constants for reaction of various nucleophiles with $S^{\bullet+}$ in methylene chloride were measured in the same manner. The data are summarized in Table I, along with the corresponding rate constants in acetonitrile. From these data it is clear that acetonitrile acts as a nucleophile in assisting the C-Si bond cleavage of the silane radical cation. As expected, however, acetonitrile is much less reactive than methanol. The rate constants in methylene chloride are approximately 3 times higher than those in acetonitrile. This solvent effect on the rate constants is analogous to that encountered in related bimolecular nucleophilic substitution reactions.[6] The substituent effects on the rate constants for the pyridine derivatives are as expected for a nucleophilic substitution. An electron donating group (4-methyl) increases the rate and an electron withdrawing group (3-chloro) decreases the rate. The 2,6-dimethyl derivative is more electron rich, but more sterically hindered for

Table II Activation Parameters for the Reaction of Various Nucleophiles with the Radical Cation of Methoxybenzyltrimethylsilane

Nucleophile	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
Acetonitrile	5.6	-16.6
Methanol	2.0	-21.2
Pyridine	1.9	-20.6

nucleophilic attack than the parent compound. These two opposing effects almost cancel each other in this case. From measurements of the decay rates of $S^{\bullet +}$ in the presence of different nucleophiles at different temperatures (3 - 70° C in acetonitrile), the enthalpies and entropies of activation summarized in Table II were obtained. The magnitude of the entropy of activation is in the expected range for an S_N2 reaction. Thus, we believe that the data presented here and in the earlier communication[5] strongly support the proposed nucleophilic-assisted cleavage of organosilane radical cations.

Since the rate of fragmentation in these reactions depend on the presence of a nucleophile, we are synthesizing organosilanes with covalently attached moities which can function as nucleophiles. Such intramolecular reactions are likely to lead to fast fragmentation even in non nucleophilic media.

ACKNOWLEDGEMENT

The authors gratefully acknowledge support from the National Science Center for Photoinduced Charge Transfer grant CHE - 8810024.

REFERENCES

1. For reviews see: (a) S. L. Mattes and S. Farid, in Organic Photochemistry; edited by A. Padwa (Marcel Dekker, New York, 1983) Vol. 6, p. 233. (b) M. Julliard and M. Chanon, Chem. Rev., 83, 425 (1983). (c) O. Hammerich, V. D. Parker, Adv. Phys. Org. Chem., 20, 55 (1984).(d) G. J. Kavarnos and N. J. Turro, Chem. Rev., 86, 401 (1986). (e) M. A. Fox, in Advances in Photochemistry, edited by D. H. Volman, K. Gollnick, and G. S. Hammond (Wiley, New York, 1986) Vol. 13, p. 237. (f) F. D. Lewis, in Photoinduced Electron Transfer Part C. Photoinduced Electron Transfer Reactions: Organic Substrates, edited by M. A. Fox and M. Chanon (Elsevier, Amsterdam, 1988) p. 1. (g) J. Mattay, Synthesis, 233 (1989).

2. I. R. Gould, D. Ege, J. E. Moser, and S. Farid, J. Am. Chem. Soc., 112, 4290 (1990).

3. For selected examples see: (a) A. Okamato, M. S. Snow, and D. R. Arnold, Tetrahedron, 42, 6175 (1986). (b) A. Albini and M. Mella, Tetrahedron, 42, 6219 (1986).(c) X. Ci and D. G. Whitten, J. Am. Chem. Soc., 111, 3459 (1989). (d) J. P. Dinnocenzo, W. P. Todd, T. R. Simpson and I. R. Gould, J. Am. Chem. Soc., 112, 2462 (1990).

4. For leading references see: (a) P. S. Mariano, in Organic Photochemistry; edited by A. Padwa (Marcel Dekker, New York, 1987) Vol. 9, p. 1. (b) W. Xu, Y. T. Jeon, E. Hasegawa, U. C. Yoon, and P. S. Mariano, J. Am. Chem. Soc., 111, 406 (1989). (c) K. Mizuno, K. Terasaka, M. Ideda, and Y. Otsuji, Tetrahedron Lett. 5819 (1985).

5. J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd, and S. L. Mattes, J. Am. Chem. Soc., 111, 8973 (1989).

6. cf. C. K. Ingold in Structure and Mechanism in Organic Chemistry (Cornell University Press, Ithaca, New York, 1953) p. 347.