Communication

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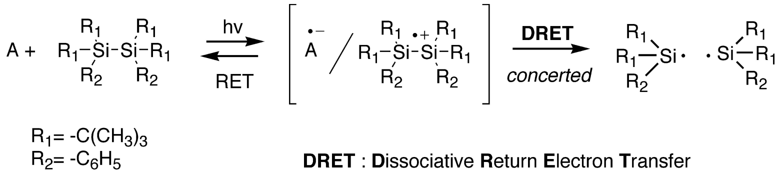

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Bond-Coupled Electron Transfer Processes: Cleavage of Si−Si Bonds in Disilanes

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Photoinduced electron transfer is a process in which an excited-state electron acceptor is reduced by an electron donor to yield a contact ion radical pair.[1] Although return electron transfer (RET) is a common energy wasting process for this species, bond-coupled electron transfer processes can effectively compete in which net chemical transformations can occur. For example, concerted dissociative return electron transfer (DRET) can produce radicals via bond fragmentation (Figure 1). We have previously investigated the mechanism details of DRET in the C−C bond cleavage and isomerization of substituted cyclopropanes.[2] In this regard, we wish to report herein our studies on other suitable substrates for DRET, in particular the Si−Si bond fragmentation in disilanes.

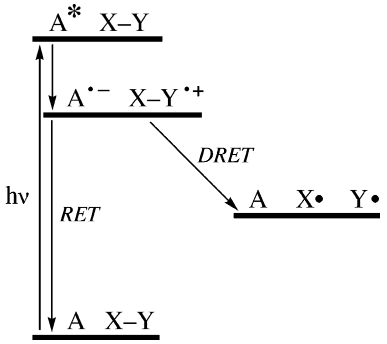
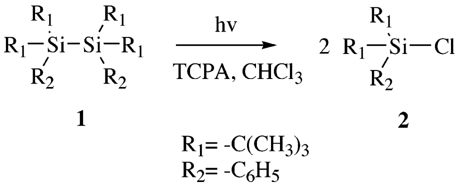


Figure 1. Schematic presentations of DRET and RET from a photochemically generated ion radical pair.

There are several factors that are important in identifying substrates that potentially will undergo DRET. First, the bond dissociation energy (BDE) of the substrate must be low enough such that an ion radical pair with sufficient driving force for DRET can be generated. Second, the oxidation potential of the substrate must be such that it can be readily photooxidized by common sensitizers. Third, oxidation of the substrate must result in significant structural changes in the cation radical with regard to the bond that is to undergo cleavage. On the basis of these factors, disilanes (and by extension oligo- and polysilanes) seemed to be ideal substrates. Although Si−Si bonds are in general moderately strong, they can be weakened by appropriate substituents as necessary.[3] In addition, disilanes are readily photooxidized,[4] and this oxidation results in electron density being removed from the Si−Si bond with concomitant elongation. For our initial studies, we have investigated disilane **1**,[5] which has a relatively low BDE, ~35 kcal/mol,[3,6] and a reasonable oxidation potential, ~1.7 V vs SCE,[7] and whose Si−Si bond undergoes elongation upon oxidation.[6]

Steady-state excitation of tetrachlorophthalic anhydride (TCPA) in dry $CHCl_3$ ($\lambda > 350$ nm) in the presence of disilane **1** (0.01 M) produced chlorosilane **2** in high chemical (>95%) and quantum ($\Phi_2 = 1.7$) yield (Scheme 1).[8−10]

Scheme 1

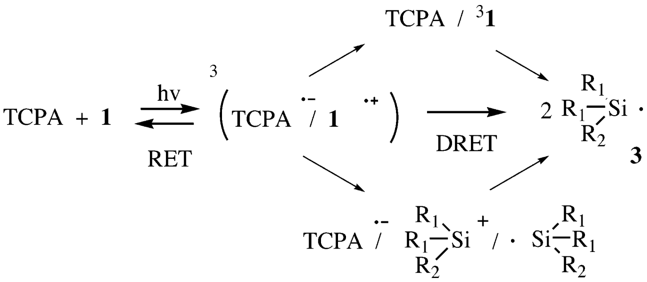


Nanosecond excitation of TCPA ($\lambda = 308$ nm) in $CHCl_3$ produces its triplet state absorption spectrum ($\lambda_{max} = 390$ nm) within the laser pulse, <20 ns. Quenching of this state, ^{3}TCPA, by disilane **1** occurs at about diffusion control, $k_q = 4.8 \times 10^9$ M^{-1} s^{-1}. Unfortunately, we could not observe any spectroscopic evidence ($\lambda > 300$ nm) for the formation of any transient species following quenching, even at higher concentrations of **1**, >0.05 M. Consequently, we can put an upper limit on the lifetime of any such transient at 20 ns, i.e., the resolution of the nanosecond laser instrument.

We believe the quenching of ^{3}TCPA by **1** occurs via electron transfer to yield the triplet ion radical pair, $^3(TCPA^{\bullet-}/\mathbf{1}^{\bullet+})$, based on energetic considerations, in which the energy of the ion radical pair, ~2.76 eV,[11] is less than that of ^{3}TCPA, 2.83 eV.[12] Quenching is inconsistent with triplet−triplet energy transfer because the energy of ^{3}**1**, ~3.4 eV, is too high to be readily accessed.[13] In addition, triplet sensitizers with high triplet state energies but more difficult to reduce, such as benzophenone, were not quenched by **1**. Unfortunately, we could not obtain any direct spectroscopic evidence for $^3(TCPA^{\bullet-}/\mathbf{1}^{\bullet+})$.

On the basis of previous work, we believe that chlorosilane **2** is formed from the reaction of di-*tert*-butylphenylsilyl radical, **3**, with the solvent $CHCl_3$ and/or CCl_4.[4,14,15] Assuming the initial formation of $^3(TCPA^{\bullet-}/\mathbf{1}^{\bullet+})$, the major mechanistic question is, how are these silyl radicals produced? Three reasonable pathways are presented in Scheme 2. The concerted DRET mechanism would yield the radicals **3** directly. However, electron transfer and Si−Si bond dissociation could occur stepwise by either (i) initial Si−Si fragmentation of $\mathbf{1}^{\bullet+}$ followed by electron transfer or (ii) initial electron transfer to yield ^{3}**1** followed by fragmentation.

Scheme 2



To exclude the possibility of initial, rapid fragmentation of $\mathbf{1}^{\bullet+}$, this species was independently generated under similar reaction conditions, but without the strong reducing $TCPA^{\bullet-}$ counterion.[16] Transient $\mathbf{1}^{\bullet+}$, λ_{max}= 370 nm, reacts with nucleophiles (CH_3OH,

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$k_q = 1.4 \times 10^7$ M^{-1} s^{-1}) and with electron transfer reagents (DABCO, $E_{ox} = 0.57$ V vs SCE),[2a] both of which are consistent with cation radical chemical reactivity. Importantly, the lifetime of **1**$^{\bullet+}$, ~500 ns, is significantly longer than that of ^{3}(TCPA$^{\bullet-}$/**1**$^{\bullet+}$), <20 ns, and consequently excludes either unimolecular or solvent-assisted bimolecular fragmentation as a viable mechanism for silyl radical **3** formation.[17] The short lifetime of the ion pair also excludes initial electron transfer to yield the localized ^{3}**1**, as this process is endothermic by ~13 kcal/mol. Consequently, DRET is the only mechanism that is consistent with our experimental observations for the formation of silyl radical **3** from the ion pair. The high efficiency of this process could be due to strong coupling of the triplet ion pair to the repulsive triplet radical pair rather than the singlet ground state.

To further explore this DRET process, several other triplet sensitizers with different reduction potentials were employed to photooxidize **1**. These sensitizers also gave high chemical yields of **2**, albeit with varying quantum efficiencies. For example, using TCPA, 3,3′4,4′-benzophenonetetra-carboxylic dianhydride (BTDA), 1,2,4,5-tetracyanobenzene (TCB), and 2,6-diclorobenzoquinone (DCQ), whose ion pair energies are 2.8, 2.7, 2.5, and 2.0 eV, the quantum yields for **2** formation are 1.7, 1.4, 0.9, and 0.6, respectively.[18] Qualitatively, we observe that as the energy of the ion radical pair is lowered, the quantum yield for **2** formation decreases, suggesting that the rate constant for DRET decreases and/or the rate constant for RET increases. These results are consistent with DRET being the operative mechanism for the formation of **2** as both DRET and RET are electron transfer reactions whose rates probably respond differently to driving force changes.

Although we have investigated disilane **1** in detail, preliminary studies suggest that DRET is quite general and is the primary pathway for Si−Si cleavage of other disilanes, oligosilanes, and polysilanes under photoinduced electron transfer conditions. Previous studies on similar substrates have suggested that Si−Si bond cleavage occurs by either unimolecular or solvent-assisted bimolecular fragmentation of the cation radical.[4,19] The corresponding cation is then reduced by the sensitizer anion radical to yield a second silyl radical that reacts with the halogenated solvent. We believe that in many of these studies, DRET may be a viable alternative mechanism for Si−Si bond fragmentation.

In conclusion, we have provided evidence for the DRET cleavage of the Si−Si bond in **1** and believe this may be a general, useful process for the fragmentation of such bonds in other di-, oligo-, and polysilanes, as well as other group 4A compounds using a variety of sensitizers with different spectral properties. Further studies will explore the effect of spin state, driving force, and substrate structure on the efficiency of this DRET process in organosilanes.

Acknowledgment. We are grateful to the National Science Foundation for research support (CHE-0111319), Dr. G. Liu for computational work, and Paul Merkel for experimental help.

Supporting Information Available: Transient absorption spectrum of **1**$^{\bullet+}$ and its decay kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Synthesis of **1**: Kusukawa, T.; Ando, W. *J. Organomet. Chem.* **1998**, *559*, 11−22.

(6) Bond dissociation energy of **1** was calculated by subtracting twice the optimized energy of the di-*tert*-butyl-phenylsilyl radical **3** from the optimized energy of **1** using B3LYP/6-31G*.

(7) (a) Determined by photoacoustic calorimetry. Goodman, J. L.; Al-Kaysi, R.; Torrence, G.; Olson, D. R. *Chem. Comm.*, submitted. (b) Zhuikov, V. V. *Russ. J. Gen. Chem.* **1999**, *69*, 1906−1911. (c) Jouikov, V. V. *Russ. Chem. Rev.* **1997**, *66*, 509−540.

(8) Quantitative analysis of **2** was performed using an HP-5840 gas chromatogram equipped with a Restek RTX-200 capillary column. Response factors were determined using hexadecane as an internal standard. Data were reproducible with less than 1% error.

(9) A second minor product is also formed, ~ 5%. On the basis of GC−MS analysis, M$^+$ = 416, we believe it might be 1,1,2-tri-*tert*-butyl-2-chloro-1,2-diphenyldisilane, formed by cleavage of the *tert*-butyl-Si bond and subsequent reaction of the radical with solvent. In addition, C_2Cl_6 and $C_2H_2Cl_4$ are also formed in CCl_4/$CHCl_3$ mixtures. TCPA is not consumed at low conversions of the disilane (<10%). However, at higher conversions, TCPA (and the other sensitizers, BTDA, TCB, and DCQ) is consumed by some unknown process.

(10) Quantum yields were determined using a standard optical bench and band-pass filters. Steady-state irradiations were carried out in argon purged dry $CHCl_3$ solution of the sensitizer and **1** (0.01 M) at 334 nm to <5% conversion of **1**. The photon flux was determined using Aberchrome-540. The quantum yield was independent of the wavelength of excitation (313, 334, 365 nm). The chemical and quantum yields of **2** were unaffected by added CCl_4.

(11) The energy of the ion radical pair TCPA$^{\bullet-}$/**1**$^{\bullet+}$ in $CHCl_3$ is estimated as the oxidation potential of **1** (1.7 V vs SCE)[7] minus the reduction potential of TCPA (−0.86 V vs SCE)[11a] and a solvent correction of 0.2 V to account for the differential solvation of the ion radical pair in $CHCl_3$ vs CH_3CN.[11b] (a) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632−3638. (b) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482−5483.

(12) (a) Sano, M.; Narisawa, T.; Matsuka, M.; l'Haya, Y. J. *Bull Chem. Soc. Jpn.* **1977**, *50*, 2266−2268. (b) We confirmed this value by low-temperature emission experiments and also determined that the quantum yield for ISC is 0.95.

(13) The emission spectrum of **1** in ethyl acetate at 77 K was obtained following 274-nm excitation. From the phosphorescence spectra, the 0−0 triplet band was observed at 360 nm, 79.4 kcal/mol.

(14) Direct photolysis of related compounds: (a) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1992**, *11*, 3731−3736. (b) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1994**, *13*, 1005−1013. (c) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 7531−7532.

(15) On the basis of the reactivity of similar silyl radicals,[14] the estimated lifetime of **3** in $CHCl_3$ precludes its direct detection. In addition, its predicted optical properties under the experimental conditions make it difficult to detect. However, quenching of ^{3}TCPA by **1** in 1,2-dichloroethane with 0.1 M chlorodiphenylmethane yields the diphenylmethyl radical, $\lambda_{max} = 336$ nm,[20] presumably by Cl abstraction by **3**.

(16) The cation radical **1**$^{\bullet+}$ was generated by photolysis of *N*-methylquinolinium hexafluoroantimonate in dry 1,2-dichloroethane/$CDCl_3$ (1:1 v/v) using toluene (2 M) as cosensitizer in the presence of the disilane (0.01 M) and oxygen to destroy the *N*-methylquinolinium radical.[15a] Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876−1883.

(17) Nucleophilic attack by $CHCl_3$ or CCl_4 on **1**$^{\bullet+}$ can be excluded because the addition (>2 M) of either halogenated solvent had little effect on the lifetime of **1**$^{\bullet+}$. In addition, the quantum yield for formation of **2** was not affected by the addition of CCl_4 (2 M). Nucleophilic attack by sensitizer anion radical on **1**$^{\bullet+}$ may occur to some extent, but this process presumably would result in a maximum quantum yield of 1 and a chemical yield of 0.5 for formation of **2**.

(18) The ion radical pair energies were calculated as in ref 11 using the reduction potentials of −0.81, −0.65, and −0.18 V vs SCE for BTDA, TCB, and DCQ, respectively.[2a]

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