

Photosensitized Reduction of Sulfonium Salts: Evidence for Nondissociative Electron Transfer

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Received August 14, 1998

Abstract: The photosensitized reductions of 4-cyanobenzylmethylphenyl sulfonium tetrafluoroborate (1-BF₄) by 9-phenylanthracene, 2-ethyl-9,10-dimethoxyanthracene, or perylene excited singlet states gives quantitative yields of phenyl methyl sulfide. Fluorescence quenching and the quantum yields for product formation, as functions of [1-BF₄], give bimolecular rate constants ($0.58\text{--}1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) for reaction of the excited sensitizers with the sulfonium salt. The limiting quantum yields, corresponding to infinite [1-BF₄], are 0.65–0.77 for the three sensitizers, revealing significant inefficiencies in the photoreduction. These inefficiencies are assigned to the partitioning of a sulfuranyl radical intermediate in a two-step associative electron-transfer mechanism.

Introduction

There is a significant body of evidence that 9-S-3 sulfuranyl radicals, [R₃S][•], are formed as reactive intermediates in the reactions of free radicals with sulfides and in the reductive cleavage of sulfonium salts. Most directly, sulfuranyl radicals with electronegative groups such as alkoxy have been observed by ESR and absorption spectroscopy.¹ In the absence of stabilizing substituents, alkyl and aryl sulfuranyl radicals are apparently short-lived and have not been observed.² Even so, indirect tests have disclosed the intermediacy of sulfuranyl radicals in a variety of reactions. In one case, a labeling study of an intramolecular free radical displacement at sulfur revealed an intermediate that partitioned among competitive pathways.³ In another case, a study of the reactions of hydrogen atoms with benzylalkyl sulfides gave different Hammett plots for the relative rates of reaction of the sulfides and the relative rates of competing benzyl versus alkyl cleavages. These results indicate that the radical addition to the sulfide and the cleavage are distinct steps, corresponding to the formation and decomposition of an intermediate sulfuranyl radical.⁴ In an especially interesting case, a [R₃S][•] intermediate was formed by free radical addition to a sulfide and trapped by oxidation.⁵ Sulfuranyl radicals are

also implicated in the reduction of sulfonium salts. Chemical experiments with potassium on graphite as the reductant showed that the relative rates of cleavage of different groups from unsymmetrical sulfonium salts depend on the specific structure of the sulfonium salts and not just on the nature of the groups being cleaved.⁶

Photochemical reductions of sulfonium salts also point to intermediate sulfuranyl radicals. For example, the quantum yield for the destruction of sulfonium salt by the photolysis of the triphenylsulfonium iodide charge-transfer complex is only 0.35.⁷ This result suggests a triphenylsulfuranyl radical intermediate that fractionates between productive fragmentation and unproductive return electron transfer.^{2,7}

The reductive cleavage of sulfonium salts can also be accomplished electrochemically.⁸ Saeva suggested that some of these reactions might proceed by a concerted mechanism.⁹ In general, the detailed characteristics of the cyclic voltammetric behavior of most sulfonium salts are in accord with a two-step “EC” mechanism—fast associative electron transfer followed by slower unimolecular fragmentation of an intermediate. In one favorable case, the oxidation of the intermediate was actually observed at high scan rates.¹⁰ On the other hand, Saeva and Saeva concluded that some phenacyl- and 4-cyanobenzyl-substituted sulfonium salts are cleaved in a dissociative mechanism; i.e., electron transfer and bond fragmentation are concerted. The stimulating conclusion that the mechanism of electrochemical cleavage can be associative (two-step) or

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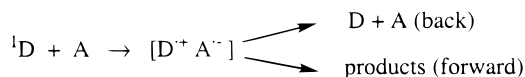
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dissociative (one-step), depending on the structure of the sulfonium salt, is not based on the direct observation of an oxidation peak in the cyclic voltammogram. For example, neither phenyldimethylsulfonium ion ("two-step") nor *p*-cyanobenzylmethylphenylsulfonium ion (**1**) ("one-step") gives reversible redox waves at scan rates up to 800 000 V/s. Rather, the mechanistic distinction is based on detailed analyses of the variations in peak potentials and peak widths as a function of scan rates.¹⁰ Savéant has argued the case for dissociative electron transfers in a number of other reductive cleavages.¹¹ There are, of course, interesting conceptual¹¹ and practical¹² implications of the idea of dissociative electron transfer.

As noted above, the reductive cleavage of sulfonium salts can also be accomplished by photoinduced electron transfer.⁷ The quantum yields for destruction of triphenylsulfonium salts with various sensitizers are routinely less than unity.^{2,7,13} The forward electron transfer can be arranged so that all of the donor excited states are captured by acceptor sulfonium salt to give the ion-radical pair. Because return electron transfer can be a very fast reaction, it can be a very demanding probe of the structure and reactions of the primary ion-radical pair. A quantum yield less than unity suggests an intermediate pair that can partition between energy-wasting (back) and productive (forward) steps¹⁴ (Scheme 1).

Scheme 1



We have used this logic¹⁵ to probe the mechanism of the reductive cleavage of 4-cyanobenzylmethylphenylsulfonium ion (**1**), the best example of a dissociative electron-transfer mechanism in the electrochemical studies.¹⁰ Our predictive distinction is that a one-step dissociative electron transfer will be revealed by a 1:1 correspondence of the destruction of excited states and the formation of cleavage products; i.e., $\Phi = 1$. A two-step associative mechanism with an intermediate that partitions will give $\Phi < 1$ (see Scheme 2). The choice of substrate is particularly important because the mechanism of electron transfer might vary with the structure of the substrate.

Results and Discussion

We studied the photoinduced reduction of 4-cyanobenzylmethylphenyl sulfonium tetrafluoroborate [**1**-BF₄] or hexafluorophosphate [**1**-PF₆] in acetonitrile using three different sensitizers, 9-phenylanthracene (PA), 2-ethyl-9,10-dimethoxyanthracene

Scheme 2

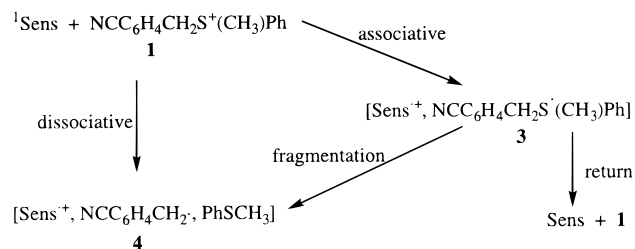


Table 1. Physical Properties of Sensitizers and **1**-BF₄

	¹ E, eV	E _{1/2} , V (Ag/AgCl)	ΔG _{ET} , eV ^d
PA	3.16 ¹⁶	1.30	-0.92
PE	2.84 ¹⁶	1.05	-0.85
EDA	3.01 ^a	0.84	-1.23
1 -BF ₄	4.4 ^b	-0.94 ^c	

^a Estimated from the midpoint of the absorption and emission spectra. ^b Estimated from the maximum of the long wavelength absorption at 284 nm. ^c Irreversible reduction: recorded value is E_P at 0.1 V/s. ^d Calculated in acetonitrile as ΔG_{ET} = E_{1/2}(sens⁺/sens) - E_P(**1**⁺/**1**^{•+}) - ¹E.

(EDA), and perylene (PE). The sensitizers were chosen to favor electron transfer and disfavor energy transfer from the excited singlet state of the sensitizer to the sulfonium salt. The appropriate physical properties are given in Table 1.

Solutions of sensitizer (~0.01 M) and sulfonium salt (~0.01 M) in acetonitrile were irradiated at wavelengths where the sensitizer absorbed, but the sulfonium salt did not. The products of the reaction are straightforward; phenyl methyl sulfide is the only sulfide formed. The other possible cleavage products, 4-cyanobenzyl phenyl sulfide and 4-cyanobenzyl methyl sulfide, could not be detected (<0.1%). Poly-4-cyanobenzylated anthracenes were identified as products of the reactions using the two anthracene sensitizers (PA and EDA). The radical cleavage product (4-cyanobenzyl radical) couples with the sensitizer cation radical to give a carbocation which is then deprotonated to give the alkylated sensitizer. This chemistry is strictly analogous to that first identified by Saeva,¹⁷ as the source of the acid in the commercially useful reactions of sulfonium salts. In addition to these important cross-coupling products, trace amounts of other products characteristic of 4-cyanobenzyl cleavage were identified in PA-sensitized reactions: 4-cyanotoluene, 4-cyanobenzyl alcohol, and 4-cyanobenzaldehyde. The dimer, 1,2-di(4-cyanophenyl)ethane, was not observed (<0.1%). *N*-(4-Cyanobenzyl) acetamide was observed in 11% yield based on phenyl methyl sulfide in reactions involving PA sensitizer, but was not formed (<0.1%) when EDA or PE were used. The formation of this interesting product will be discussed later. Finally, 2-ethyl-9,10-anthraquinone was observed in reactions using EDA as a sensitizer. A related dealkylation path was identified previously and attributed to reactions of the dialkoxyanthracene cation radical.¹⁸ The photosensitized reactions were analyzed by ¹H NMR as a function of photolysis time. As shown in Figure 1a,b, there is a 1:1 correspondence between the destruction of the sulfonium salt and the formation of phenyl methyl sulfide. Accordingly, the formation of phenyl methyl sulfide was used to monitor the photoreduction reaction.

Flash photolysis of solutions of PA in acetonitrile gives readily detectable yields of ¹PA (590 nm) and ³PA (430 nm).¹⁹

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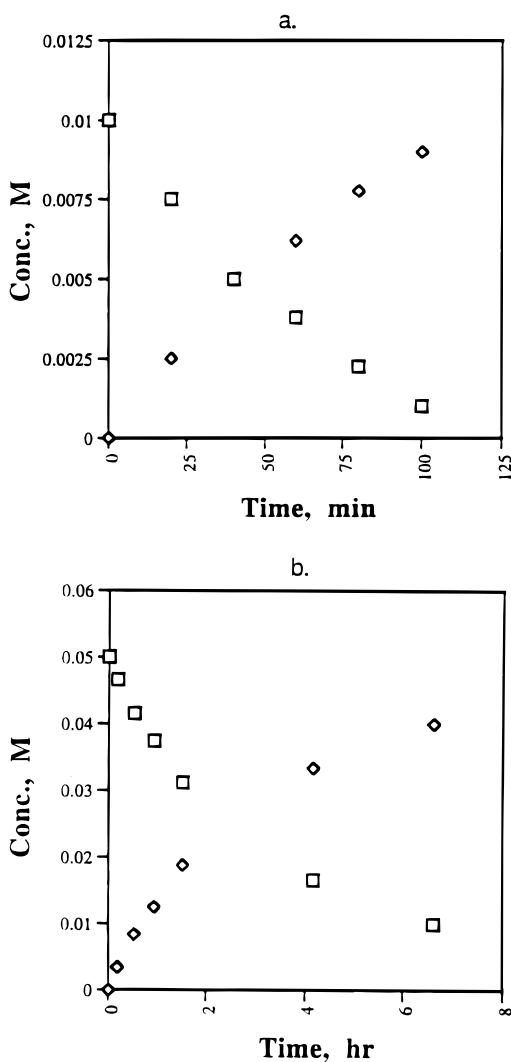


Figure 1. Concentrations of 4-cyanobenzylmethylphenyl sulfonium salt [1-BF₄] (□) and phenyl methyl sulfide (◇) as a function of photolysis time: (a) PA sensitizer; (b) EDA sensitizer.

The rate of disappearance of ¹PA was markedly accelerated by low concentrations of sulfonium salt 1-BF₄, while the rate of decay of ³PA was unchanged. Strong fluorescence in acetonitrile was easily observed for all three sensitizers; the fluorescence intensity decreased when the sulfonium salt 1-BF₄ was added to each solution of the sensitizers. These quenching processes followed the Stern–Volmer equation, $F_0/F = 1 + k_q\tau_0[1]$, where F is the emission intensity integrated across the band. A typical relationship is shown in Figure 2, and the results are summarized in Table 2. Fluorescence lifetimes were measured by single-photon counting under the same (nondeoxygenated) conditions used for the Stern–Volmer analyses. These lifetimes are reported in Table 2 also. The Stern–Volmer slopes and the observed lifetimes give the quenching constants, k_q . These k_q values are consistent with near-diffusion-controlled quenching of the excited sensitizers by 1-BF₄ ($k_{diff} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in CH₃CN at 25 °C).¹⁶ Similar results were obtained in the quenching of ¹PA by 1-PF₆ ($k_q = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and the corresponding ethyl derivative, 2-PF₆ ($k_q = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

The quenching process could also be monitored by studying the lifetime of the fluorescent state as a function of the

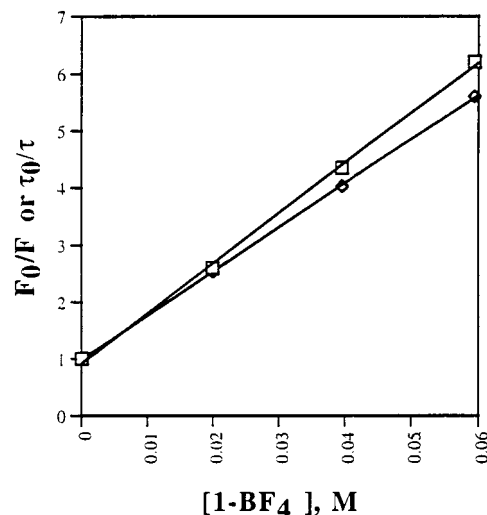


Figure 2. Stern–Volmer analyses of fluorescence and lifetime quenching of ¹EDA by 1-BF₄: □ = F_0/F ; ◇ = τ_0/τ .

Table 2. Results of Stern–Volmer Analyses of Fluorescence Quenching by 1-BF₄

sensitizer	λ_{ex} , nm ^a	λ_{em} , nm ^b	$k_q\tau_0$, M ⁻¹	r^c	τ_0 , ns ^d	$10^{-10} k_q$, M ⁻¹ s ⁻¹
PA	362	380–500	49.66	0.9998	5.1	0.97
PE	380	400–600	50.83	0.9997	4.6	1.10
EDA	383	390–550	87.36	0.9994	8.2	1.07

^a Wavelength of exciting radiation. ^b Wavelength of emission band. ^c Correlation coefficient. ^d Nondeoxygenated solutions.

concentration of sulfonium salt. This experiment, with EDA as the sensitizer, is also shown in Figure 2. The good agreement between these two different experiments shows that the dominant quenching process is dynamic and that there is no significant contribution from ground state complex formation. Spectra of mixtures of each sensitizer with sulfonium salt in acetonitrile showed no new absorptions in the UV region, leading to the same conclusion. As part of the fluorescence quenching studies, we also searched carefully for new fluorescence emissions; no new emissions were observed.

Since there is a 1:1 correspondence of the disappearance of the sulfonium salt to the appearance of phenyl methyl sulfide, the quantum yield for the two processes must be the same. Because the reaction of the sensitizer singlet with sulfonium salt is a dynamic process, the observed quantum yield for the formation of phenyl methyl sulfide is a function of the concentration of sulfonium salt. Plots of $1/\Phi_{obs}^{PhSCH_3}$ vs $1/[1-BF_4]$ were linear for all three sensitizers, Figure 3. The slopes, in conjunction with the sensitizer singlet lifetimes measured under the same conditions, give the bimolecular rate constants for the reactions of the sensitizer singlets with sulfonium salt. These rate constants are in acceptable agreement with those derived from fluorescence quenching. The intercepts of the plots give the limiting quantum yields, corresponding to the quantum yield when 100% of the sensitizer singlets are captured by reaction with the sulfonium salt. Values of τ_0 , k_q , and Φ_{LIM} are reported in Table 3.

As outlined in the Introduction, our mechanistic distinction is that a concerted, dissociative electron transfer should give a correspondence of excited states captured to cleavage product formed, i.e., $\Phi_{LIM}^{PhSCH_3} = 1$. In contrast, electron transfer to give an intermediate that can partition between paths that do and do not give phenyl methyl sulfide will be inefficient, $\Phi_{LIM}^{PhSCH_3} < 1$. The observed values of $\Phi_{LIM}^{PhSCH_3}$ for three different sensitizers

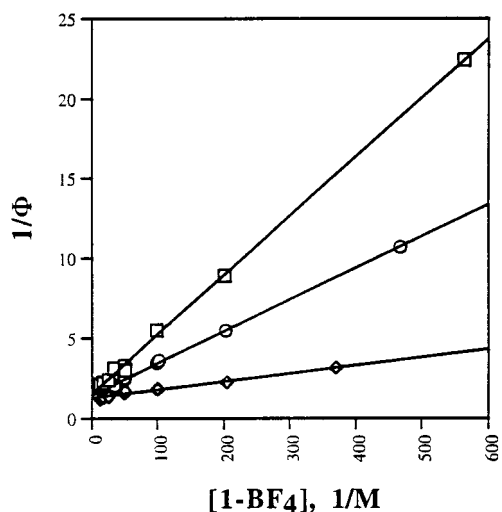


Figure 3. Stern–Volmer analysis of the yield of phenyl methyl sulfide as a function of [1-BF₄]: □ = 9-phenylanthracene; ◇ = 2-ethylidimethoxyanthracene; ○ = perylene.

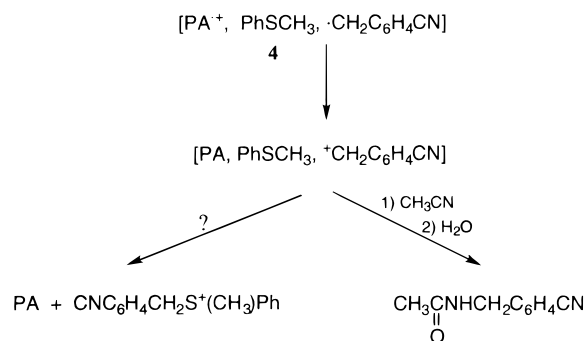
Table 3. Results of Stern–Volmer Analyses of Product Formation from the Reactions of ¹Sensitizers with Sulfonium Salt 1-BF₄

sensitizer	τ_0 , ^a ns	$10^{10}k_q$, M ⁻¹ s ⁻¹	$\Phi_{\text{LIM}}^{\text{PhSCH}_3}$	ΔG_{BET} , eV ^b
PA	7.2	0.58	0.65 ± 0.003	-2.2
PE	5.9	1.2	0.69 ± 0.01	-2.0
EDA	16.1	1.6	0.77 ± 0.02	-1.8

^a Deoxygenated solutions. ^b Calculated from $\Delta G = E_p(1^+/1^\bullet) - E_{1/2}(\text{sens}^{*\bullet}/\text{sens})$.

are all less than one, providing *prima facie* evidence for a two-step mechanism involving an intermediate. Stated differently, the mechanism of the photosensitized reductive cleavage of the sulfonium salt provides an opportunity for the energy of the incident light to be wasted. The rates, energetics, and products of the reactions reported here and those of closely related reactions^{2,12–14} are all in accord with a photoinduced electron transfer from sensitizer donor to sulfonium acceptor to give the primary intermediate, **3**, in Scheme 2. Since the system is arranged so that all of the light is absorbed by the sensitizer and all of the sensitizer excited singlets are captured by the sulfonium salt, and since there is no path for destruction of sulfonium salt that does not give phenyl methyl sulfide, the trivial sources of inefficiency are ruled out. Accordingly, the source of the inefficiency must be in the partitioning of the primary intermediate. The absence of any new emission indicates the absence of a radiative pathway for **3** to return to sulfonium salt. On the other hand, nonradiative return electron transfer would waste the incident energy and regenerate the starting material. As recorded in Table 3, the return electron transfer is strongly exoergic in all three cases. Accordingly, return electron transfer is expected to be a fast, sensitive probe of the structure of the primary intermediate. The quantum yields reveal a competition between reversion to starting sulfonium ion and formation of product; i.e., the rate of the forward reaction of the primary intermediate **3** must be comparable to the rate of the return electron-transfer reactions. From our data, it is not possible to determine whether this forward rate is for fragmentation of the sulfuranyl radical within the primary cage to give a secondary intermediate, **4**, or for diffusive separation of the components of the primary cage. However, the photo-CIDNP results on the sensitized photoreductions of diphenyliodonium and triphenylsulfonium salts in CD₃CN do permit a distinction.² Both Ph₂I⁺ (return electron transfer) and C₆H₅D

Scheme 3



(forward reaction) are polarized to give emission. This result is best interpreted^{2b} in terms of successive caged radical pairs; the partitioning of the primary intermediate [Ph₂I⁺, sens^{*+}] is responsible for the polarization of Ph₂I⁺ and the partitioning of the secondary intermediate [PhI, Ph^{*}, sens^{*+}] is responsible for the net emissive polarization in C₆H₅D. The photosensitized CIDNP experiment with Ph₃S⁺ still gives evidence for successive radical pairs, but fails to directly reveal the sulfuranyl radical; C₆H₅D is polarized in emission, but polarized Ph₃S⁺ is not observed. The rate for diffusive separation in acetonitrile is a reference clock for the return electron transfer and the fragmentation rates. Both return and fragmentation are sufficiently fast to compete successfully with diffusive separation,²⁰ indicating rate constants > 10⁹ s⁻¹. These rate constants are more than an order of magnitude greater than the limit set by the absence of an oxidation wave in the cyclic voltammogram at high scan rates (> 4 × 10⁷ s⁻¹).¹⁰

The formation of some 4-cyanobenzylacetamide (10% yield) in the phenylanthracene-sensitized reaction of the sulfonium salt stimulated us to think of a roundabout mechanism for wasting the photochemical energy. The formation of the amide signals the formation of 4-cyanobenzyl cation, which is captured by acetonitrile and water to give the observed amide. One might imagine that the initial electron transfer is actually concerted to give directly the caged partners **4**. Electron transfer from the 4-cyanobenzyl radical ($E_{1/2}^{\text{ox}} = 1.08$ V, SCE)²¹ to the 9-phenylanthracene cation radical ($E_{1/2}^{\text{ox}} = -1.13$ V SCE)²² within the cage would give the 4-cyanobenzyl cation, which could then be captured by phenyl methyl sulfide to regenerate the starting sulfonium ion. According to this hypothetical mechanism (Scheme 3), the source of the inefficiency is a “three-step” process in which phenyl methyl sulfide is the species that partitions. However intriguing this mechanism might be, it cannot be a generalized source of the photochemical inefficiencies because no 4-cyanobenzylacetamide can be detected (< 0.1%) in the reactions sensitized by EDA or PE. In fact, these other sensitizers were chosen because the corresponding cation radicals are less oxidizing (PE, -0.85 V, SCE;¹⁶ EDA, -0.66 V, SCE) than the cation radical derived from phenylanthracene. A related “reassembly” mechanism for energy wasting could involve initial dissociative electron transfer to give the caged partners, **4**. “Reaction” of these partners with concomitant electron transfer would give back sulfonium ion **1** and the sensitizer ground state. The implication of the forward dissociative electron transfer is that the sulfuranyl radical is not an

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energy minimum.^{23,24} Accordingly, the sulfuranyl radical cannot be involved in the return process; i.e., the return reaction would have to be an “associative electron transfer”. Although such a process is conceptually valid,²⁵ it is unprecedented.

One might imagine yet another source of inefficiency. Suppose that the sulfonium salt reacts with ¹sens not only by electron transfer, but also catalyzes some intersystem crossing of ¹sens to ³sens. The energetics of electron transfer from ³sens to sulfonium salt are unfavorable²⁶ and ³sens would, therefore, simply decay nonradiatively to the ground state. In this hypothetical scenario, it is the excited singlet state of the sensitizer that fractionates. This intersystem crossing was previously excluded for PA by spectroscopic experiments.^{2a} Clearly, the best way to settle the question of the 9-S-3 intermediate is to observe it. We attempted to detect the primary intermediates, **3**, for each sensitizer by picosecond absorption spectroscopy, but failed to observe any new well-defined absorptions that could be assigned to a sulfuranyl radical. The “intersystem crossing” mechanism described above requires a significant yield ($\Phi \approx 0.2$ – 0.3) of sensitizer triplets, followed by slow unimolecular decay of the triplets. This process would have been easily detected in nano- and picosecond absorption experiments with perylene since the intersystem crossing yield in the absence of sulfonium salt is only 1%. In the presence of sulfonium salt **1**-BF₄, the absorption of ¹PE (710 nm) was decreased with no concomitant increase in the absorption of [³PE] at 480 nm.

Conclusion

The experiments and the logic outlined here rule out alternative sources of inefficiency in the reactions of sensitizer singlet excited states with 4-cyanobenzylmethylphenyl sulfonium salt, the “best-case” candidate for dissociative electron

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(26) The energies¹⁶ of ³PA (1.82 eV) and ³PE (1.57 eV), in conjunction with the redox potentials in Table I, lead to the conclusion that ΔG_{ET} is +0.42 eV for both ³PA and ³PE.

transfer in the electrochemical studies. The most consistent interpretation of the observed inefficiencies is that the electron transfer is not concerted and that short-lived 9-S-3 sulfuranyl radicals are involved as intermediates in the photosensitized reductive cleavage reactions of sulfonium salts.²⁷ The important implication of this conclusion is that considerations of the characteristics of these reductive cleavages must, necessarily, involve considerations of the structures, stabilities, and relative rates of formation and fragmentation of the sulfuranyl radical intermediates.

Acknowledgment. This research was supported by the National Science Foundation Center for Photoinduced Charge Transfer, CHE-9120001. We are especially grateful to Professor Joshua L. Goodman for an extended series of instructive discussions

Supporting Information Available: Experimental details for the preparation and characterization of sulfonium salts **1**-BF₄ and **1**-PF₆, **2**-BF₄, and **2**-PF₆, for the characterization of photolysis products, and for photochemical measurements, including a table of quantum yields for the formation of PhSCH₃ as a function of [**1**-BF₄] (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA982932X

(27) Whether there is a contradiction between the electrochemical and the photochemical observations remains to be seen. Savéant has discussed other cases (e.g., CF₃Br, ArCH₂Br) where different modes of reduction have led to different conclusions about the mechanism of the reductive cleavage.^{10,11} Some of the differences were attributed to environmental effects (solvation, ion pairing) that stabilize an anion radical intermediate and thereby favor a stepwise path. Those factors are presumably not important in the case of a neutral sulfuranyl radical intermediate. Alternatively, Savéant has argued that the mechanism can change as a function of the driving force. Just such a crossover was reported for benzylphenylmethylsulfonium ion; increasing driving force (scan rate) led to a decrease in the cyclic voltammetric peak width that was attributed to a change in mechanism from concerted to stepwise.¹⁰ In the present case, the argument would be that the lower driving force in the electrochemical reduction of 4-cyanobenzylmethylphenyl sulfonium salt favors the concerted mechanism and the larger driving force in the photochemical reduction favors the stepwise mechanism. More recently, Roberts and Savéant have invoked an avoided crossing model to rationalize the different mechanistic conclusions derived from photochemical and electrochemical experiments.²⁸

(28) Robert, M.; Savéant, J.-M., 1999, submitted for publication. We are grateful to Professor Savéant for sharing a preprint with us.