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Bimolecular Photoreduction of Aromatic Sulfoxides

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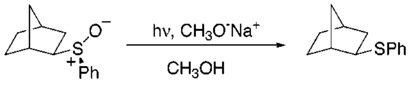
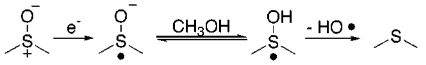
Photolysis of aromatic sulfoxides in the presence of alkoxides in alcoholic solvents provides a photochemical route to the corresponding sulfides. Other electron donors also give sulfide with various degrees of success. The reaction could also be carried out using carbazoles as sensitizers, and quantitative yields could be obtained using *N*-methylcarbazole in methanol. Evidence points toward a hydroxysulfuranyl radical as the key intermediate, and solvent effects point to heterolysis, rather than homolysis, as the step that breaks the S−O bond.

Introduction

The reduction of sulfoxides to sulfides may be accomplished with a variety of reagents.[1−5] The photochemical reduction of sulfoxides, however, has not received a great deal of attention. In this paper, we report a study of this reaction, which is as notable for being a member of the rare class of bimolecular photochemical reactions of sulfoxides as for its potential synthetic utility.

Unimolecular photochemical deoxygenation of sulfoxides is a known process that occurs with low quantum yield.[6−10] The sulfide is usually only a major product if α-cleavage chemistry is suppressed by structural factors. Good chemical yields have been obtained in a few instances.[6] Bimolecular photochemical reduction of sulfoxides was mentioned by Kropp in a study designed to investigate whether certain cleavage reactions of aromatic sulfides were homo- or heterolytic.[11] In the presence of 200 mM sodium methoxide in methanol, norbornyl phenyl sulfide was produced in yields up to 64% on photolysis of the corresponding sulfoxide. In the absence of methoxide, only a trace of sulfide was produced. The mechanism proposed by Kropp involved formation of a 9-S-3 hydroxysulfuranyl radical, followed by homolysis to give the sulfide. In this paper, we report several experiments designed to test this mechanism and expand the scope of the reaction.

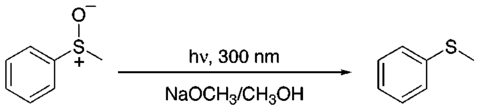




Results

Most of the experiments described below involve photolysis of solutions containing a sulfoxide and an additive or sensitizer, followed by analysis of the reaction mixture. Unless otherwise noted, solutions were approximately 5 mL samples, photolyzed through quartz after having been sealed under a septum and flushed with Ar to remove molecular oxygen. Samples were analyzed either by HPLC or by GC. *p*-Xylene and dodecane were used as internal standards, respectively.

Alkoxide/Alcohol Solvent Systems. To replicate the results of Kropp, where an alkyl phenyl sulfoxide was studied, methyl phenyl sulfoxide **1** was chosen as a model starting material.



1 **2**

Solutions of 10 mM **1** and the desired concentration of $NaOCH_3$ were prepared in methanol. Solutions were photolyzed using the broadly emitting 300 nm fluorescent bulbs of a Rayonet minireactor, and yields were determined by HPLC (Figure 1). Control experiments without methoxide produced only trace quantities of thioanisole (**2**). The low concentration methoxide runs showed that methoxide was not consumed stoichiometrically. The downward curvature in yields is due to secondary photolysis of **2**.

One conceivable decomposition pathway of a hydroxysulfuranyl radical is by loss of the elements of water. Thus, it was next determined if there was a requirement for a hydrogen adjacent to the sulfinyl group by use of diphenyl sulfoxide (**3**) as a substrate. In experiments otherwise identical to those reported in Figure 1, the

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[1] Drabowicz, J.; Numata, T.; Oae, S. *Org. Prep. Proc. Int.* **1977**, *9*, 63−83.

[2] Drabowicz, J.; Togo, H.; Mikolajczyk, M.; Oae, S. *Org. Prep. Proc. Int.* **1984**, *16*, 171−98.

[3] Madesclaire, M. *Tetrahedron* **1988**, *44*, 6537−80.

[4] Kukushkin, V. Y. *Coord. Chem. Rev.* **1995**, *139*, 375−407.

[5] Kukushkin, V. Y. *Rus. Chem. Rev.* **1990**, *59*, 844−52.

[6] Gurria, G. M.; Posner, G. H. *J. Org. Chem.* **1973**, *38*, 2419−20.

[7] Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 217−28.

[8] Jenks, W. S.; Gregory, D. D.; Guo, Y.; Lee, W.; Tetzlaff, T. In *Organic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1, pp 1−56.

[9] Still, I. W. J. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappaport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons Ltd.: New York, 1988; pp 873−87.

[10] Gregory, D. D.; Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 94−102.

[11] Kropp, P. J.; Fryxell, G. E.; Tubergen, M. W.; Hager, M. W.; Harris Jr., G. D.; McDermott Jr., T. P.; Tornero-Velez, R. *J. Am. Chem. Soc.* **1991**, *113*, 7300−10.

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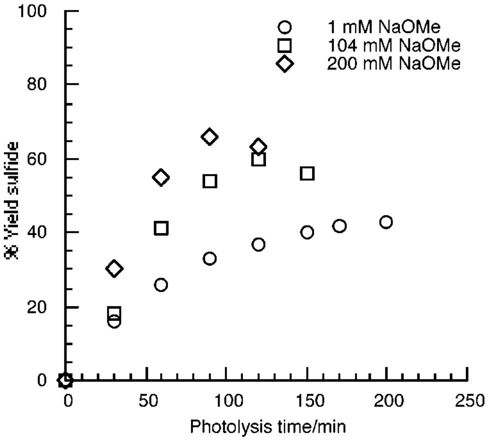

Figure 1. Yield of sulfide **2** as a function of photolysis time and methoxide concentration. The initial concentration of **1** was 10 mM in CH_3OH.

Table 1. Reduction of 3 in MeOH/NaOMe[a]

photolysis time (min)	1 mM NaOMe		200 mM NaOMe	
	% yield	% conversion	% yield	% conversion
30	25	43	78	93
60	41	58	58	97
90	43	72		

[a] Percent yield of diphenyl sulfide (**4**) and percent conversion of **3** as a function of sodium methoxide concentration in methanol, using 300 nm excitation. The starting concentration of sulfoxide was 10 mM.

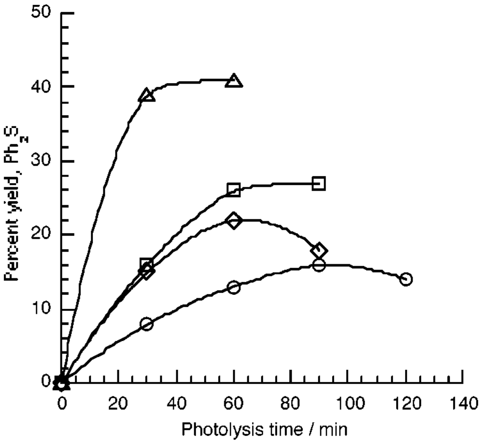

Figure 2. Yield of diphenyl sulfide from photolysis of **3** under various conditions in *t*-BuOH. Circles: $[CH_3OH] = 0$ mM, $[t\text{-BuONa}] = 162$ mM, 59% conversion at 120 min; diamonds: $[CH_3OH] = 81$ mM, $[t\text{-BuONa}] = 80$ mM, 74% conversion at 90 min; squares: $[CH_3OH] = 41$ mM, $[t\text{-BuONa}] = 160$ mM 78% conversion at 90 min; triangles: $[CH_3OH] = 164$ mM, $[t\text{-BuONa}] = 67$ mM, 97% conversion at 60 min. The curves are arbitrary.

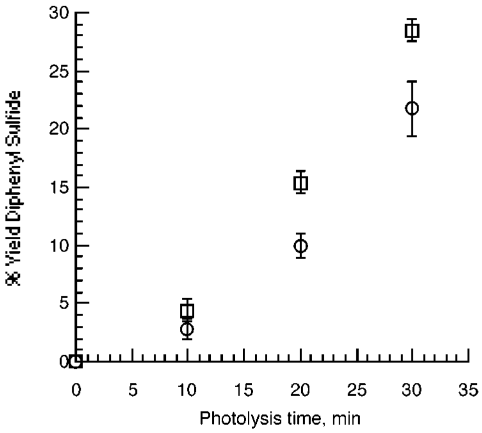

Figure 3. Yield of Ph_2S from *t*-BuOH solutions containing 40 mM **3**, 100 mM KOH, 10 mM dodecane, and 100 mM CH_3OH (squares) or CD_3OD (circles). Error bars are standard deviations for runs in triplicate.

appearance of diphenyl sulfide was monitored (Table 1), and it was shown that **3** was an acceptable, or even superior, substrate. Disappearance of the sulfoxide was also monitored, and it became clear that secondary photolysis of the sulfide product under these conditions lowered the observed yield at the highest conversions.

The reduction reaction was repeated in *tert*-butyl alchohol, using the corresponding conjugate base. To ensure the melting point of the solvent would be well below room temperature, 1% H_2O (by volume) was added. With 160 mM *t*-BuONa,[12] only a maximum of 16% yield of sulfide **4** was produced after 90 min of photolysis. Surprisingly modest quantities of methanol as an additive restored most of the usual reactivity, as shown in Figure 2.

In another set of experiments, instead of water being added to the *t*-BuOH to keep it from freezing, 1% anhydrous ether was added. There were two notable results. First, the yields of sulfide were very similar to the case where methanol was used as the additive (approximately 50% yield at at 90% coversion). Second, virtually no additional effect was noted when methanol (up to 320 mM) or water (1 vol %) was added to the solutions that already contained 1% ether.

Finally, the effect of using CD_3OD instead of CH_3OH as additive was investigated. Solutions in *t*-BuOH were prepared containing 40 mM **3**, 100 mM KOH, 10 mM dodecane, and 100 mM of either CD_3OD or CH_3OH. Solutions were run in triplicate to ensure reproducibility. As shown in Figure 3, the CH_3OH-doped solution provided **4** in higher quantum yield than did the CD_3OD-doped solution. (The sulfoxide consumption was also slower with CD_3OD.) The error bars represent standard deviations for the samples run in triplicate.

Potential Quenchers Aside from Alkoxides/Hydroxide. A set of experiments that utilized aniline or pyridine was undertaken to determine if the specific presence of RO^- was required, or if the alkoxide was acting as an electron-transfer agent that could be replaced. Pyridine and aniline were chosen as alternate bases to alkoxide. Since the pK_B values of the two bases are similar, 9.4 for the former and 8.8 for the latter,[13] both compounds would be expected to deprotonate methanol to similar very small extents, but only aniline is a good electron donor. Samples were prepared with 10 mM **1** and 100 mM of the amine in methanol. The samples were photolyzed using the 254 nm irradiation from unfiltered low pressure mercury tubes. This change in wavelength was to allow absorption of most of the light by the sulfoxide. Only trace sulfide was observed when

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(12) Clearly, hydroxide is an important species here when water is present, but we use the alkoxide nomenclature for clarity.

(13) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972.

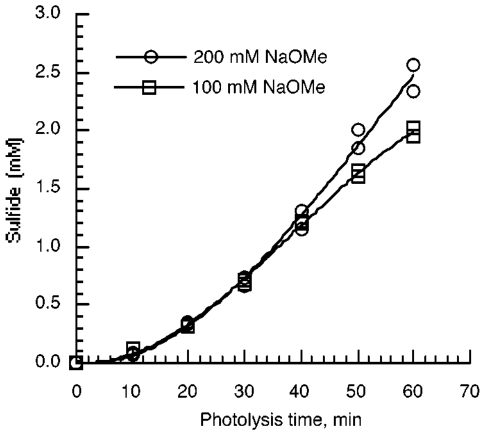

Figure 4. Yield of diphenyl sulfide from diphenyl sulfoxide as a function of photolysis time. Starting sulfoxide concentration is 10 mM, irradiation is at 254 nm.

pyridine was used, but aniline provided moderate yields of sulfide **2**.

Alternative oxidizable additives were tried. A solution of triethylphosphine (10 mM), sulfoxide **1** (1.0 mM), and dodecane (0.56 mM) in methanol was prepared in an oxygen-free glovebox. Photolysis of this solution at 254 nm provided a 30% yield of sulfide at 90% conversion. The corresponding phosphine oxide was observed in GC runs, but it could not be determined whether this was an artifact of the analytical method. Triphenylphosphine was also used as a potential electron donor. Under similar conditions, a 10% yield of sulfide was observed at 90% conversion of sulfoxide. It should be noted that most of the light was absorbed by Ph_3P, but see below for related experiments. Dibutyl sulfide and triethylamine were explored as reducing agents without success.

Quantum Yields. To measure the quantum yield of the photoreduction of **3**, further experiments were carried out using 254 nm excitation. Because the potential products have extinction coefficients a few times as large as **3** at 254 nm, it was particularly desirable to conduct these measurements to low conversion. The results are shown in Figure 4. An induction period is clearly observed, followed by a period of relatively linear growth of sulfide concentration. This made measurements with very small conversions impractical.

The appearance of this induction period caused examination of the effect of molecular oxygen. If, instead of Ar flushing, solutions were saturated with O_2, formation of sulfide was almost completely suppressed and consumption of the sulfoxide was also significantly curtailed. In the absence of methoxide, quantum yields for loss of the sulfoxides are lower, but O_2 affects only the product mixture[14] without changing the rate of sulfoxide consumption. That oxygen quenched the sulfoxide reduction reaction suggested that the induction period shown in Figure 3 might be due to residual molecular oxygen not removed by Ar flushing. Photolyses were carried out on samples that were treated by freeze−pump−thaw degassing, but the induction period remained.

It was then suspected that the induction period might come from impurities, so very carefully prepared solutions were used. Freshly prepared sodium methoxide (200 mM) and diphenyl sulfoxide (10 mM) that had been multiply recrystallized until no impurities were observable by GC were dissolved in methanol. Dodecane was used as an internal standard. The optical transparency of the methoxide solutions was checked before solutions were prepared. A 100 mL solution, purged with Ar, was irradiated at 254 nm for 180 min. Samples of 0.5 mL were removed every 10 min through a septum, diluted with water (0.5 mL), and exctracted with ether (1.0 mL). The ether extract was then analyzed by GC. Even these measures failed to rid the initial 10% of conversion from having an upward curvature.

Table 2. Qualitative Quantum Yields for Photolysis of Diphenyl Sulfoxide in Methanol.

[NaOMe], mM	Φ_{SO}[a]	Φ_S[b]
200	0.103	0.045
100	0.079	0.035
50	0.047	0.037

[a] Quantum yield for disappearance of sulfoxide. [b] Quantum yield for appearance of sulfide. Values should be treated with caution. See text.

Eventually, the induction period was accepted as unavoidable, whether inherent or due to residual oxygen or impurities. The slope of product formation in the approximately linear portion (e.g., approximately 20−50 min in Figure 2) was used to get at least a qualitative handle on quantum yields.

Sensitized Reductions. In light of the positive results using aniline as a reducing agent, *N*-methylaniline and *N*,*N*-dimethylaniline were investigated as well. It was hypothesized that the methylated derivatives might be better oxidants in that the iminium salts could be products and that demethylated aniline products could be observed. It was quickly found that the broad 300 nm irradiation would be concentrated on the aniline, rather than the sulfoxide. This turns the reaction into a sensitized one from the perspective of the sulfoxide.

Solutions were prepared containing **3** (10 mM) and either *N*-methylaniline (10 mM) or *N*,*N*-dimethylaniline (10 mM). After 2 h irradiation, *N*-methylaniline solution was at 85% sulfide yield with 85% sulfoxide conversion, whereas the *N*,*N*-dimethylaniline solution was at 65% sulfide yield with 65% sulfoxide conversion. Control experiments showed that O_2 again quenched the reaction. Demethylated aniline products were not observed, but several other small unidentified peaks appeared to derive from sensitizer degradation.

The effects of solvent on the reduction process with the aniline sensitizers were evaluated. The reduction of diphenyl sulfoxide (10 mM) was carried out with *N*-methylaniline (20 mM) in methanol, methanol spiked with 1% water, in dry THF, and in THF spiked with 1% water. The sample with methanol spiked with water produced sulfide in 90% yield at 90% conversion, quite similar to the “dry” methanol sample. Dry THF solution only produced 58% sulfide at 90% conversion. The wet THF sample was marginally better than the dry THF sample (66% yield of sulfide at 90% conversion).

Quantum yields for diphenyl sulfide apperance (Φ_s) with *N*-methylaniline as an electron donor as a function of solvent were determined (Table 3). No induction period was observed. Samples containing **3** (10 mM), *N*-methylaniline (10 mM) in methanol, acetonitrile, or THF were prepared. Photolysis was carried out at 313 nm, using excitation from a Xe lamp filtered through a monochromator, to ensure anilines absorbed the light.

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(14) Guo, Y.; Jenks, W. S. *J. Org. Chem.* **1997**, *62*, 857−64.

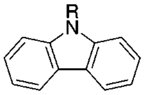
Table 3. Quantum Yield of the Appearance of Diphenyl Sulfide with *N*-Methylaniline as Sensitizer, Using 313 nm Irradiation

solvent	Φ_s
MeOH	0.48
MeCN	0.34
THF	0.41

Table 4. Quantum Yield of the Appearance of Diphenyl Sulfide Using *N*-Methylcarbazole 6 as Sensitizer in Methanol.

conditions	Φ_s
10 mM **3**, 10 mM **6**	0.38
200 mM **3**, 20 mM **6**	0.95

Carbazoles **5**, **6**, and **7** were also used as sensitizers in the reduction of diphenyl sulfoxide. Photolyses were carried out with using black light bulbs (emission centered at 350 nm) in the Rayonet mini-photoreactors unless otherwise noted. This ensured that only the carbazoles absorbed the light. All three of the carbazoles had extinction coefficients of at least 3000 M^{-1} cm^{-1} at 340 nm. All solutions, unless otherwise noted, contained sulfoxide **3** (10 mM) and a carbazole **5**, **6**, or **7** (10 mM).



5: R = H
6: R = CH_3
7: R = CH_2CH_3

Control experiments showed that smaller concentrations of carbazoles could be used, but the reactions were generally faster with high sensitizer concentrations, so most reactions were carried out that way. Quantum yields were measured using **6** and 313 nm irradiation, as shown in Table 4.

It was found qualitatively that 9-methylcarbazole **6** produced the best yield of sulfide, but that carbazoles **5** and **7** were similar. In acetonitrile, however, the parent carbazole **5** produced sulfide much more efficiently than either of the other two sensitizers, with **7** producing virtually none.

Aliphatic sulfoxides tetramethylene sulfoxide and dibenzyl sulfoxide were resistant to reduction by carbazole. Standard solutions of 10 mM sulfoxide and 10 mM sensitizer in methanol were prepared. Tetramethylene sulfoxide was intert to photolysis using the black lights under these conditions for 3 h, but dibenzyl sulfoxide showed a modest amount of decomposition by α-cleavage routes.[15]

Nature of the Carbazole Sensitization. The photophysics of the carbazole chromophore have been studied carefully.[16] Triplet yields are generally relatively large and two-photon photoionization is known. Carbazoles are also well-known as electron donors, and at least *N*-ethylcarbazole is known to show radical cations in flash photolysis spectra in polar solvents in the absence of any other quenchers.[17] Thus, in principle, the sulfoxides might be interacting with singlets, triplets, or solvated electrons generated from photolysis of the carbazole. Each of these possibilities were addressed.

Table 5. Rates of Quenching of a Solvated Electron by Various Sulfoxides.

compound	$k_{\mathrm{r},}$ 10^9 M^{-1} s^{-1}
dibenzothiophene oxide	9.5
diphenyl sulfoxide	9.1
di(*p*-chlorophenyl) sulfoxide	7.6
di(*p*-bromophenyl) sulfoxide	7.2
di(*p*-methoxyphenyl) sulfoxide	4.7
p-methoxyphenyl methyl sulfoxide	2.4
dibenzyl sulfoxide	2.0
dimethyl sulfoxide	0.012

Table 6. Rate Constants for Quenching of Carbazole Fluorescence by Various Sulfoxides at Room Temperature in Acetonitrile.

	$k_{\mathrm{q},}$ 10^9 $\mathrm{M}^{-1}\mathrm{s}^{-1}$		
sulfoxide	carbazole	*N*-methyl-carbazole	*N*-ethyl-carbazole
diphenyl sulfoxide	5.0	5.2	2.2
di(*p*-fluorphenyl) sulfoxide		3.4	
di(*p*-fluorphenyl) sulfoxide		7.0	
dibenzothiophene sulfoxide		6.2	
dibenzyl sulfoxide		0.15	

The plausibility of sulfoxide reaction with solvated electrons in the polar solvents was shown by the rate constant data in Table 5. The electrons were generated by photoionization of *N*,*N*,*N′N′*-tetramethyl-*p*-phenylenediamine in acetonitrile using the 355 nm output of a ns Nd:Yag laser.[18] The relative concentration of the solvated electron was monitored by its well-known broad absorption spectrum in the visible region. While sulfoxide radical anions were not explicitly observed, the lifetimes of the solvated electrons were sensitive to sulfoxide concentration. These rate constants are in excellent agreement with values of 9.1×10^9 M^{-1} s^{-1} for **3** and 3.7 10^6 M^{-1} s^{-1} for *n*-Bu_2SO in aqueous solutions.[19]

Given that concentration changes in a range of 10−200 mM affected the quantum yield as seen in Table 4, it was plausible that the carbazole singlet was involved. Singlet quenching rate constants (Table 6) were determined by monitoring the fluorescence lifetime of the carbazoles as a function of sulfoxide concentration, using the time-correlated single photon counting method. Dibenzyl sulfoxide, a control compound that did not suffer reduction under any investigated conditions, produced a rate constant for quenching at least an order of magnitude lower than all the others.

Triplet sensitization by energy transfer by carbazoles is not plausible, given the triplet energies of carbazole ($E_T \sim 70$ kcal/mol)[20] and simple aryl sulfoxides (∼80 kcal/mol).[21] Nonetheless, electron transfer might be mediated through long-lived triplets. Addition of isoprene ($E_T \sim 60$ kcal/mol)[20] at concentrations up to 10 mM to solutions containing 2 mM **3** and 2 mM **6** did not affect the quantum yield, thus eliminating triplet-based chemistry.

Higher Concentrations and the Consumption of Sensitizers. Several reactions were run at high sulfoxide concentration and sensitizer concentration to examine degradation of the sensitizers. The anililine reactions all

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[15] Kharasch, N.; Khodair, A. I. A. *J. Chem. Soc., Chem. Commun.* **1967**, 98−100.

[16] Bonesi, S. M.; Erra-Balsells, R. *J. Lumin.* **2001**, *93*.

[17] Haggquist, G. W.; Burkhart, R. D.; Naqvi, K. R. *J. Phys. Chem.* **1991**, *95*, 7588−94.

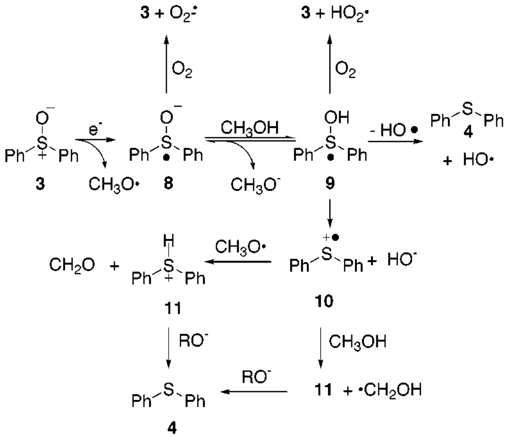
[18] Alkaitis, S. A.; Grätzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 3549−55.

[19] Engman, L.; Lind, J.; Merényi, G. *J. Phys. Chem.* **1994**, *98*, 3174−82.

[20] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; 2nd ed.; Marcel Dekker: New York, 1993.

[21] Jenks, W. S.; Lee, W.; Shutters, D. *J. Phys. Chem.* **1994**, *98*, 2282−9.

Scheme 1



yellowed with conversion and were thus candidates. Samples with initial concentrations of 40 mM and 15 mM of **3** and *N*-methylaniline, respectively, were prepared in methanol and acetonitrile. After formation of approximately 20 mM **4**, significant degradation of the *N*-methylaniline was noted. In acetonitrile, ~5 mM sensitizer had disappeared, and in methanol ~10 mM sensitizer had disappeared. In both cases, only very tiny new GC peaks appeared, but significant discoloration of the solutions was observed. Similarly, discoloration was noted in the solutions using **5** as sensitizer. New solutions containing 40 mM **3** and 5 mM **5** were prepared, also in acetonitrile and methanol. After formation of about 12 mM **4**, about 2.5 mM carbazole had disappeared from the acetonitrile solution and about 1.5 mM carbazole had disappeared from the methanol solution.

Discussion

Photolysis of phenyl methyl or diphenyl sulfoxide at 300 nm with sodium methoxide in methanol produces reasonable yields of the corresponding sulfides, in good agreement with the original findings of Kropp.[11] The notion of electron transfer initiation of the reduction reaction clearly stands up, especially in light of the successful use of more classic electron transfer agents. We have extended the reaction to include milder conditions and the use of sensitizers that absorb considerably to the red of the sulfoxides, which may enhance the utility of this chemistry.

Qualitatively speaking, the carbazoles are the sensitizers of choice and methanol the solvent of choice among those we investigated. First, the relatively low energy absorption spectrum is not interfered with by many reasonable starting materials or products and quantitative sulfide yields can be obtained. *N*-Methylcarbazole does not degrade significantly during the reaction. The anilines can also produce sulfide in excellent yield, but the sensitizers tend to degrade somewhat during the course of the reaction and higher energy irradiation must be used. The original formulation, where the sulfoxide is irradiated in the presence of high concentrations of methoxide may have its applications, but the low quantum yield and harsh conditions seem to make the other conditions more attractive.

We consider an expanded view of the Kropp mechanism as outlined in Scheme 1. Excitation of the sulfoxides provides approximately 4 eV energy, which should be sufficient to effect electron transfer to form **8**. We believe the singlet lifetimes of **1** and **3** are likely to be short, based on precedent from other aromatic sulfoxides, in which sulfoxide singlet lifetimes were roughly 1 order of magnitude smaller than those of the parent arenes.[22] These sulfoxides are not fluorescent, so we were unable to measure quenching rate constants, but such short lifetimes are consistent with the modest quantum yields reported in Table 2 and their apparent dependence on alkoxide concentration in a very high range.

The pK_a of $(CH_3)_2SOH\bullet$ has been estimated at about 17 by independent groups.[23,24] Thus, at least in the alcoholic solvents or alcohol/water mixtures, it is reasonable to expect that the radical ion **8**, once formed, will be protonated by solvent to give the hydroxysulfuranyl radical **9**.

Dialkylhydroxysulfuranyl radicals (e.g., **9**) have been the subjects of study in other contexts. Though other types of 9-S-3 sulfuranyl radicals are persistent,[25,26] acyclic dialkylhydroxysulfuranyls are but reactive intermediates. In the gas phase, reaction of dimethyl sulfide with HO• produces $(CH_3)_2SOH\bullet$.[27−29] While there has been controversy over the topic, both experimental and computational approaches have recently converged on an S−O homolytic bond dissociation energy of about 11 kcal/mol.[30,31] In contrast, the universally reported fate of $(CH_3)_2SOH\bullet$ in aqueous solution is heterolytic dissociation to $(CH_3)_2S^{\bullet+}$ and HO^-.[23,24,26] The estimated $\Delta G°$ for this process is about 5 kcal/mol,[24] and the hydroxydialkylsulfuranyl radicals are often not directly observed because of their rapid decomposition. An estimate of <7 kcal/mol has been made for the homolytic S−O bond strength of **9**, but solvation in water would again be expected to favor heterolysis to **10**, as is experimentally observed.[19,32] The difference between the gas and solution phase decomposition routes is directly related to the solvation of ions. It is thus reasonable to postulate that in alcoholic solvents, the difference between homolysis and heterolysis may be smaller than in water, and homolysis may be favored in some of the solvents, such as THF.

For the moment, though, we restrict the discussion to the case of alkoxide base in alcoholic solvents. Both the heterolytic and homolytic pathways are catalytic in base; this does not distinguish the mechanisms. The solvent effects, however, may present a resolution. The reaction is less efficient in *t*-BuOH than in methanol. Given that the *t*-BuOH samples contained water, this is unlikely to be due to the protonation step (i.e., **8** to **9**), especially given the effects of methanol and ether as additives. If it is posited that the major decomposition pathway of the

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[22] Lee, W.; Jenks, W. S. *J. Org. Chem.* **2001**, *66*, 474−80.

[23] Chaudhri, S. A.; Mohan, H.; Anklam, E.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1996**, 383−90.

[24] Merenyi, G.; Lind, J.; Engman, L. *J. Phys. Chem.* **1996**, *100*, 8875−81.

[25] Martin, J. C.; Perkins, C. W.; Clarkson, R. B. *J. Am. Chem. Soc.* **1986**, *108*, 3206−10.

[26] Margaretha, P. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1999; pp 277−88.

[27] Hynes, A. J.; Stoker, R. B.; Pounds, A. J.; McKay, T.; Bradshaw, J. D.; Nicovich, J. M.; Wine, P. H. *J. Phys. Chem.* **1995**, *99*, 16967−75.

[28] Barone, S. B.; Turnipseed, A. A.; Ravishankara, A. R. *Faraday Discuss.* **1996**, *100*, 39−54.

[29] Barone, S. B.; Turnipseed, A. A.; Ravishankara, A. R. *J. Phys. Chem.* **1996**, *100*, 14694−702.

[30] Turecek, F. *Collect. Czech. Chem. Commun.* **2000**, *65*, 455−76.

[31] McKee, M. L. *J. Phys. Chem.* **1993**, *97*, 10971−6.

[32] Three electron adducts of radical cationic dimers of aryl sulfides are not observed, though they are quite common for dialkyl sulfides.

sulfide radical cation (i.e., **10** to **11**) is by reaction with another radical, then it might be expected that methanol would be a better solvent than *t*-BuOH, since disproportionation with *t*-BuO• would be considerably less favorable than with CH_3O•. If instead, **10** decomposes mainly by hydrogen abstraction from solvent, methanol is more favorable as a hydrogen atom donor than is *t*-BuOH. The very poor yield of sulfide in *t*-BuOH is consistent with multiple radical decomposition pathways, as might be predicted in either case.

Modest quantities of methanol might improve the overall reaction efficiency in *t*-BuOH by the following sequence of reactions:

$$t\text{-BuO}\bullet + CH_3OH \rightarrow t\text{-BuOH} + \bullet CH_2OH$$

$$\mathbf{10} + CH_3OH \rightarrow \mathbf{11} + \bullet CH_2OH$$

$$\mathbf{10} + \bullet CH_2OH \rightarrow \mathbf{11} + CH_2O$$

$$\mathbf{11} + RO^- \rightarrow \mathbf{4} + ROH$$

$$2\bullet CH_2OH \rightarrow CH_2O + CH_3OH$$

To the extent that CD_3OH slowed the first of these reactions and the butoxyl radical did other unfavorable chemistry that did not lead to formation of **4**, an isotope effect is expected. Similarly, to the extent that the alternative reaction between **10** and methanol is slowed by deuteration, the yield of **4** could drop. This sequence also is consistent with the "additive effect" of diethyl ether being approximately equivalent to that of methanol. It is a reasonable hydrogen atom donor, and ethyl vinyl ether would be produced as the sacrificial oxidation product rather than formaldehyde.

Radical cation **10** might react with either methanol or other radicals, such as •CH_2OH. The S−H bond strength of **11** is not known, but we estimate[33] that of $PhMeSH^+$ to be 78 kcal/mol, about 17 kcal/mol less than methanol.[34] That of Ph_2SH^+ should be similar or a little lower. Depending on the precise activation parameters for the radical-methanol reaction and the steady-state concentration of the reactive intermediates, the competition between these two pathways might be tipped in either direction.[35]

To invoke homolytic cleavage of **9** to **4** and hydroxyl radical, one must come up with a more convoluted explanation of the methanol isotope effect. Of course, since the yields (even taking account of unconverted starting material) are not quantitative, one can invoke various unobserved processes. An alternative would be to suggest that the homolysis is coupled to hydrogen abstraction by the nascent HO• in the transition state, but this seems suspect intuitively, given the very modest bond strengths involved.

Any variation on these themes is consistent with quenching of the reaction by O_2. In aqueous solution, O_2 reacts with $(CH_3)_2SOH$• at 2×10^8 $M^{-1}s^{-1}$.[24] In the gas phase, the reaction of O_2 and $(CH_3)_2SOH$• is known to produce DMSO and HOO•.[36] In our experiments, this would look like quenching the reaction, since it would return the intermediate to starting material. O_2 is also expected to react with the radical anion **8** to give superoxide ($O_2^{\bullet -}$) and **3** at nearly diffusion controlled rates.[24] All of these scenarios result in the consumption of molecular oxygen, and it thus remains possible that the induction period illustrated in Figure 4 is due to trace adventitious oxygen, despite our efforts. When methoxide is not present within the sample, oxygen saturation does not particularly suppress the photochemistry (which occurs in lower quantum yield). However, it produces a different ratio of products when compared to an argon degassed sample, but these products are due mainly to singlet α-cleavage chemistry that produces radicals in small quantum yield.[14]

Next we consider the reaction in alcoholic solvents using alternative quenchers to the alkoxides. Anilines, carbazoles, and phosphines are all thermodynamically capable of reducing **3** to **8** when either the sulfoxide or the additive is excited by UV light. However, so is triethylamine. We must assume that back electron transfer is more efficient in some cases, though it is unsatisfying to do so with little other evidence. For the anilines and carbazoles, after electron transfer, proton transfer from the N−H or C−H to **8** is expected, given the reduced pK_as of radical cations.[37,38] From *N*-methylaniline, for example, this would yield **8** and $PhNHCH_2$•.

The C−H bond strength of simple alkylated anilines is in the low 90s kcal/mol,[39] quite comparable to that of the C−H bond in methanol, about 95 kcal/mol.[40] Thus, if dissociation of **9** is rapid, then reaction between methanol and the radicals derived from *N*-methylaniline, *N*,*N*-dimethylaniline, or *N*-methyl- or *N*-ethylcarbazole is likely to produce •CH_2OH as in Scheme 1, while regenerating the sensitizer.

$$\text{Sens}\bullet + CH_3OH \rightarrow \text{Sens-H} + \bullet CH_2OH$$

$$\bullet CH_2OH + \mathbf{10} \rightarrow CH_2O + \mathbf{11}$$

The NH bond strengths of aniline and carbazole are in the same range, though the exact literature values differ slightly.[37,38,41] This transient involvement of sensitizer-derived radicals is also consistent with the gradual decomposition of the sensitizers.

It is known that pyridine rapidly quenches carbazole singlets nonradiatively and produces the carbazolyl radical by H-atom transfer when quenching the triplet in cyclohexane.[42,43] It is possible that sulfoxides may act in the same manner, though in methanol the situation may be more ambiguous. Regardless, formation of **9** from carbazole photolysis, whether in a single step or two,

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[33] Calculated from the ionization potential and proton affinity of thioanisole, and the ionization potential of a hydrogen atom.

[34] *NIST Chemistry Web Book. NIST Standard Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; NIST: Gaithersburg, MD; July 2001 release.

[35] The pseudo-first-order rate constant is about 500 s^{-1} for reaction with methanol, adopting a 17 kcal activation energy, log $A = 13$ and a methanol concentration of 10 M. The pseudo-first-order rate constant for the radical−radical reaction is about 10^3 if one adopts a second-order rate constant of 10^9 and a concentration of 1 μM.

[36] Turnipseed, A. A.; Barone, S. B.; Ravishankara, A. R. *J. Phys. Chem.* **1996**, *100*, 14703−13.

[37] Bordwell, F. G.; Zhang, X.; Cheng, J. P. *J. Org. Chem.* **1991**, *56*, 3216−9.

[38] Bordwell, F. G.; Zhang, X.-m.; Cheng, J. P. *J. Org. Chem.* **1993**, *58*, 6410−6.

[39] Dombrowski, G. W.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Org. Chem.* **1999**, *64*, 427−31.

[40] Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750−65.

[41] Jonsson, M.; Lind, J.; Eriksen, T., E.; Merényi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423−7.

[42] Martin, M., M.; Ware, W. R. *J. Phys. Chem.* **1978**, *82*, 2770−6.

[43] Martin, M. M.; Breheret, E. *J. Phys. Chem.* **1982**, *86*, 107−11.

seems quite likely, and the source of the proton is at least in a net sense likely to be the carbazole itself.

The matter of what exactly the sulfoxide interacts with on photolysis of carbazoles can be addressed. Though the data in Table 5 show that quenching of the solvated electron is plausible, we believe this to be unlikely because the observed quantum yields are an order of magnitude higher than the reported quantum yield for cation formation by **7** under flash photolysis conditions, and our steady state irradiation is much less likely to produce two-photon chemistry.[17] The isoprene experiments appear to eliminate the carbazole triplet state, so by process of elimination, we conclude that carbazole singlets are quenched. In Table 6, it is shown that the interaction is near the diffusion controlled limit. The natural fluorescent lifetime of the *N*-methylcarbazole is, depending on the conditions, in the range of 15−17 ns. This represents a total decay rate of about 6×10^7 s^{-1}. The measured rate constant for diphenyl sulfoxide quenching is 5×10^9 M^{-1} s^{-1}. Given a high efficiency for all other steps, at 10 mM sulfoxide, this predicts a quantum yield just under 0.5. It also predicts a notably higher quantum yield when higher sulfoxide concentrations are used. Indeed, as shown in Table 4, a quantum yield of 0.38 is observed at 10 mM, and a quantum yield of 0.95 is seen at 200 mM. Using the same rate constant data, a value of 0.94 is predicted. The precision of the similarity of data is probably coincidental, but is quite consistent with singlet quenching. Rapid formation of **9**, followed by rapid heterolytic dissociation could easily account for the observed efficiency.

While methanol was the solvent of choice, reactions were also successful in THF. Here, all of the sensitizers must be acting as proton donors for the **8** to **9** step, since there the solvent does not inherently provide acidic protons. Like methanol, THF is a hydrogen atom donor that presumably is the ultimate reducing agent when it is the solvent, providing dihydrofuran instead of formaldehyde.

The acetonitrile case is harder to rationalize. First, there is the huge difference in reactivity between the successful sensitizer **5** and the unsuccessful derivatives **6** and **7**. The obvious difference between them is the source of the proton, being NH versus CH. Perhaps the proton transfer is concerted (or nearly so) with the electron transfer, while back electron transfer dominates with the other sensitizers. However, this difference was not important in THF where external protons are also not available. It seems unlikely, however, that the difference is due to homolytic cleavage in acetonitrile with heterolytic cleavage elsewhere.

Furthermore, the stoichiometric reducing agent in acetonitrile is not obvious. Acetonitrile itself is a very poor kinetic hydrogen atom donor. After heterolysis of **9**, the sensitizer radical and the sulfide radical cation remain, a combination that does not appear favorable for product formation and sensitizer recovery. A possibility is that the sulfide radical cations disproportionate in the presence of the hydroxide to generate a single molecule of sulfide and return the other to sulfoxide. This is at least consistent with the quantum yields below 0.5, but that evidence is circumstantial at best. Some degradation of the anilines is observed, but is much less than stoichiometric. (If homolysis of **9** occurs, the sulfide is formed, but then the sensitizer radical and hydroxyl radical remain.) One must tentatively conclude that acetonitrile must not be an inert solvent in this chemistry.

Conclusions

The dramatic increase in sulfide yield observed by Kropp for the photolysis of phenyl norbornyl sulfoxide in the presence of sodium methoxide has been substantiated by numerous experiments. Data consistent with and expanding upon Kropp's proposed mechanism were presented here. The data are consistent with a heterolytic dissociation of the putative hydroxysulfuranyl radical, but a homolytic dissociation cannot be entirely ruled out. The reduction can be carried out with varying degrees of success using other reducing agents such as aniline and triethylphosphine.

The reduction may also be carried out in such a manner that the sulfoxide does not absorb the light, but an electron-donating sensitizer such as aniline or a carbazole derivative does. The subsequent mechanistic steps should be analogous to those in the original methoxide/methanol conditions. The most practical system observed for possible synthetic utility appears to be the use of *N*-methylcarbazole as the sensitizer, with high concentration of sulfoxide in methanol. This provides for high quantum and chemical yield, along with relatively red-shifted absorption of the sensitizer. The data are most consistent with singlet-based electron-transfer chemistry in this case.

Experimental Section

General Instrumentation. ^{1}H and ^{13}C NMR were obtained on a Varian VXR-300 MHz spectrometer. HPLC data were collected with a HP 1050 liquid chromatograph with diode array detector. An ODS Hypersil reverse phase column (5 μm, 200×2.1 mm, Hewlett-Packard) was used. Eluents consisted of an acetonitrile/water gradient. UV spectra were obtained on a Shimadzu UV-2101 PC UV−vis scanning spectrophotometer. GC data were collected on an HP/5890 series II GC and a Phenomenex Zebron ZB-5 (5% Phenyl Polysiloxane) capillary column (30 m × 0.25 mm I.D. × 0.25 mm FT) was employed. Fluorescence lifetimes for the singlet quenching experiments were collected on an Edinburgh Instruments FL-900 single photon counting fluorometer.

General Methods. Response factors (±10%) for sulfoxides and sulfides were determined against the internal standard *p*-xylene for HPLC and dodecane for GC. Quantum yields (±20%) were obtained by using the actinometer azoxybenzene.[44] The flash photolysis experiments were carried out on an apparatus that has been described before.[45] Excitation was provided by a ns Nd:Yag laser operating at 355 nm. The spectrum of the solvated electron was collected for verification before any kinetics runs were performed, and then the kinetics were observed at the maximum of the absorption. Each rate constant represents at least five different concentrations of sulfoxide. Though there is probably a 10−15% uncertainty associated with the rate constants, the relative order of the quenchers was reproducible.

Reagents. All solvents were obtained as the highest grade commercially available (HPLC grade when possible) and used as received except as noted. Sodium methoxide was used as received in some preliminary experiments, and then prepared from solid sodium and HPLC grade methanol for the rest. Aniline, *N*-methylaniline, *N*-dimethylaniline, *N*,*N*-dimethylaniline, triethylamine, trimethyl phosphite, and di-*n*-butyl

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(44) Bunce, N. J.; LaMarre, J.; Vaish, S. P. *Photochem. Photobiol.* **1984**, *39*, 531−3.

(45) Darmanyan, A. P.; Gregory, D. D.; Guo, Y.; Jenks, W. S. *J. Phys. Chem. A* **1997**, *101*, 6855−63.

sulfide were distilled before use. Triethylphosphine was transferred in a glovebox to a septum-sealed vial under argon. Triphenylphosphine was recrystallized from hexanes twice before use, and the carbazoles were recrystallized from ethanol. Alkoxides were prepared from sodium metal and the corresponding alcohol. Diphenyl sulfoxide was recrystallized from ethanol. Sulfoxides other than **1** and **3** were obtained as previously described.[21]

Photolyses. Unless otherwise noted, all solutions were flushed with Ar to remove oxygen prior to photolysis. Two different photolytic systems were utilized in these experiments. The most commonly used was the Southern New England Ultraviolet Rayonet minireactor equipped with 8 × 4W fluorescent lamps. This reactor had been modified to contain both a fan and a magnetic stirrer. The fan maintained the photoreactor at ambient temperature. All reported photolyses were stirred for homogeneous photolysis. Low pressure mercury lamps either using the main emission at 254 nm or coatings that emit broadly around 300 and 355 nm were used as described in the text. For the photolyses in the Rayonet minireactor, 12 mm diameter quartz test tubes were used in conjunction with a merry-go-round sample holder to ensure uniform irradiation. The standard sample size was 5 mL unless otherwise noted.

The second system employed a 150 W Xe lamp and monochromator from Photon Technologies, Inc. The monochromator was used to select the desired photolysis wavelength, and slit widths allowed for ± 12 nm linear dispersion. Photolyses utilizing the monochromator were performed using standard sealable square 1 cm quartz cells with magnetic stirring.

The samples containing large quantities of alkoxide base were subjected to mini-workups before analysis. Samples of approximately 0.1 mL were extracted by syringe. For HPLC analysis, they were neutralized with a saturated methanolic NH_4Cl solution before injection. For GC analysis, small extractions of approximately 0.5 mL of ether and 0.5 mL of saturated aqueous NH_4Cl were performed before injection.

Photolyses of carbazole, aniline, and phosphine systems were analayzed by GC with samples taken by syringe and then shot directly onto the GC. The carbazole and aniline systems were generally contained 10 mM sulfoxide, 5 mM dodecane as an internal standard, and 10 mM carbazole or aniline except as noted. The phosphine systems were run at 2 mM sulfoxide, 2 mM phosphines, and 0.5 mM dodecane as an internal standard.

Quantum yields were determined using azoxybenzene as an actinometer[44] and the Xe lamp with the monochromator as the light source, adjusted to the desired wavelength. The photon flux was determined using a stirred solution of azoxybenzene of known volume and sufficient concentration to absorb all of the light exiting the monochromator. The samples were similarly of known volume and suficient concentration to absorb all of the exiting light, so that the slope of the initial phase product formation (moles vs time) can be used to determine the quantum yield. All reported quantum yields represent averages from multiple runs.

Single Photon Counting Measurements. All luminescence lifetimes were measured at ambient temperature. Queching rate constants were by measurement of the fluorescence lifetime of 9-methylcarbazole (or **5** or **7**) as a function of diphenyl sulfoxide concentration (excitation wavelength = 353 nm, emission wavelength = 396). Samples were prepared in methanol with ~1 mM carbazole and 0−2.5 mM sulfoxide and purged with argon for 10 min.

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