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Generation and Decay of Aryl Sulfinyl and Sulfenyl Radicals: A Transient Absorption and Computational Study[1]

Alexander P. Darmanyan, Daniel D. Gregory, Yushen Guo, and William S. Jenks*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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Absorption spectra and extinction coefficients of phenylsulfinyl and phenylsulfenyl (thiyl) radicals are determined by nanosecond laser photolysis in various solvents. Direct observation and characterization of arylsulfinyl radicals from the photolysis of several aromatic sulfoxides provides the strongest evidence to date for α-cleavage as the predominant primary photochemical process for these compounds. The absorption spectrum of phenylsulfinyl, with $\lambda_{\max} = 300$ and 450 nm and $\epsilon = 1.1 \times 10^4$ and 1.3×10^3 M^{-1} cm^{-1}, is practically independent of solvent. Quantum yields of free sulfinyl radicals range from 0.09 to 0.18 in various solvents. Recombination rate constants very near diffusion control indicate that there is a large spin−orbital coupling in the radical pair. Rate constants for the reactions of arylsulfinyl radicals with stable nitroxide radicals are among the fastest known, but reactivity with O_2 is very modest. Computations indicate that the singly occupied molecular orbital is a π^* orbital largely localized on the sulfur and oxygen atoms.

Introduction

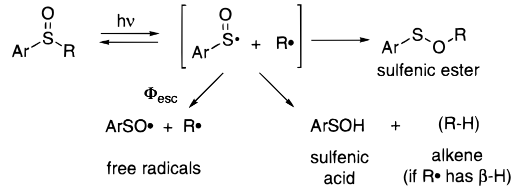
One of the common mechanistic assumptions in sulfoxide photochemistry is that the primary step after excitation is homolytic α-cleavage of one of the C−S bonds to form a radical pair or biradical.[2−24] Recently we have carefully examined a series of aryl alkyl sulfoxides by steady state photolysis techniques and found that nearly all of the observed chemistry could be accounted for by α-cleavage to form a carbon centered radical and arylsulfinyl radical. Cleavage is followed by competition between diffusional separation of the radical pair to form free radicals, recombination to form sulfoxide, and recombination to form sulfenic ester (Scheme 1).[23] Other secondary reactions, such as hydrogen abstraction by the radicals, are made available by variation of the sulfoxide precursor structure.[24]

Beyond their incidence in sulfoxide photochemistry, smaller sulfinyl radicals, notably $HSO^{\bullet}$ and $CH_3SO^{\bullet}$, are of interest because of their involvement in atmospheric sulfur cycles.[25,26] They are implicated in the oxidations of H_2S, CH_3SCH_3, CH_3SSCH_3, and CH_3SH.[27] $HSO^{\bullet}$, for instance, has been proposed to lie along the pathway from $HS^{\bullet}$ to atmospheric H_2SO_4 by way of reaction with ozone.[28−32] It has also been unambiguously demonstrated that $CH_3SO^{\bullet}$ is an intermediate in the gas phase photolysis of dimethyl sulfoxide.[33]

In this paper we report a solution phase transient absorption study of aryl sulfoxide photolysis designed to characterize directly the proposed arylsulfinyl radical intermediate **1**. Extinction coefficients and absolute rate constants for reactions of **1** have been determined, and structural information can be retrieved from ab initio and density functional calculations.

Some physical evidence for sulfoxide α-cleavage in solution (beyond conclusions drawn from product study) was previously available. This took the form of weak EPR signals of sulfinyl radicals at low temperature[34−37] and chemically induced dynamic nuclear polarization (CIDNP) signals attributed to the intermediacy of sulfinyls.[38−40] However, overinterpretation of such data without corroborating evidence can be misleading as they do not necessarily indicate radical pathways for the majority of material. Only a brief and qualitative report of a transient absorption spectrum attributed to phenylsulfinyl has appeared previously.[41] This, however, served as sufficient evidence to begin a quantitative characterization of the arylsulfinyl spectroscopy and reactivity that is reported herein. We have also carried out a computational study on the structure of phenylsulfinyl, designed to help elucidate the meaning of the two resonance forms shown for **1**.

SCHEME 1



The chemistry of arylsulfenyl radicals **2** has been characterized much more thoroughly than that of arylsulfinyl radicals. Picosecond regime recombination of geminate $PhS^{\bullet}$ radical pairs in hydrocarbons has been reported.[42] The full absorption spectrum of $PhS^{\bullet}$ was determined in water ($\lambda_{\max} = 295$ and 460 nm; $\epsilon = 1.0 \times 10^4$ and 2.5×10^3 M cm^{-1}),[43] and several rate constants for reactions of $PhS^{\bullet}$ are known, including an extensive set of studies on the reversible reactions of $PhS^{\bullet}$ with olefins.[44,45] Summarizing very briefly, $PhS^{\bullet}$ reactivity follows a trend expected for an electrophilic species. No magnetic field effects were observed on Φ_{esc} values for $PhS^{\bullet}$ in micelles, which was attributed to large spin−orbital coupling (SOC) in the radical pairs,[46] consistent with calculations locating the unpaired spin localized on the sulfur atom.[47] We report the absorption spectrum, extinction coefficients, quantum yields, and absolute rate constants for recombination of $PhS^{\bullet}$ in organic solvents in addition to the data for $ArSO^{\bullet}$ species.

Experimental Section

Spectroscopy. All experiments were carried out using a computer-controlled nanosecond transient absorption spectrometer. The samples were irradiated with the fourth harmonic of a Continuum Surelite Nd:YAG laser (266 nm, 5 ns, 2−25 mJ/pulse, 3 mm beam radius). The spectroscopic detection system includes a pulsed 75 W xenon lamp ($\tau \sim 1$ ms), an ISA H10 monochromator, an 1P-28 photomultiplier ($R_l = 50\ \Omega$), and a

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Textronix TDS-250 200 MHz transient digitizer. Control of the experiment, data collection, and processing were carried out using a Macintosh with Labview 2 software. The laser beam was used at 90° with respect to the probe beam. Investigations were carried out in a quartz flow cell $1 \times 1 \times 5$ cm or in a regular quartz cell where solutions were changed after one or two laser pulses because of extensive photodecomposition. When it was necessary, the decay kinetics were averaged for several laser pulses. The optical densities of solutions were ~0.3 at 266 nm. The accuracy of quantum yields, ϵ, and various rate constants is estimated to be ±20%. Except for reactions with O_2, rate constants were determined from lifetimes observed at no fewer than five quencher concentrations.

Absorption spectra of solutions were recorded on a UV-2101 PC Shimadzu spectrophotometer. The solutions were deoxygenated by Ar bubbling or saturated with O_2 when required for 20 min. Experiments were carried out at ambient temperature, approximately 25 °C.

Solvents. Spectrograde solvents were used as received. The 2-methyl-2-propanol, which though not spectrograde did not contain any interfering absorbances, was treated with 1% (by volume) water to prevent freezing. Water was produced with a Millipore Milli-Q UVPlus deionizer.

Materials. Diphenyl sulfoxide (**5**) was obtained commercially and recrystallized from ethanol. Diphenyl disulfide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), di-*tert*-butyl nitroxide (DTBN), and galvinoxyl were used as received from commercial sources. The preparation of phenyl *tert*-butyl sulfoxide (**6**), benzyl phenyl sulfoxide (**8**, X = H), and benzyl *p*-tolyl sulfoxide (**8**, X = CH_3) have been described previously.[23,24]

Phenyl Diphenylmethyl Sulfoxide (7). The sulfoxide was prepared in 60% isolated yield by oxidation of the sulfide with the urea−hydrogen peroxide complex followed by column chromatography on silica.[48] ^{1}H NMR ($CDCl_3$): δ 7.23−7.39 (m, 15 H), 4.80 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 77.8, 125.0, 128.2, 128.5, 128.6, 128.8, 129.3, 129.7, 131.1, 134.1, 135.5, 142.9. Analysis of the ^{13}C NMR intensities clearly indicated that one of the peaks represented two diastereotopic carbons, but it was not determined which of several it was.

The sulfide was prepared by modification of the method of Finzi and Bellavita.[49] Benzhydrol (11 g, 59 mmol) was dissolved in 75 mL acetic acid and 25 mL of sulfuric acid at room temperature. To this mixture, thiophenol (59 mmol) was added in a dropwise fashion. After 2 h of stirring, the mixture was filtered, and the precipitate was washed thoroughly with water and then dried. This provided 14.4 g (59 mmol) of the sulfide of sufficient purity to carry on the oxidation. ^{1}H NMR ($CDCl_3$): δ 7.40 (d, J = 7.2 Hz, 4 H), 7.12−7.30 (m, 11 H), 5.53 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 57.3, 126.5, 127.2, 128.4, 128.5, 128.7, 130.4, 136.1, 141.0.

Benzyl *p*-chlorophenyl sulfoxide (8, X = Cl) was prepared in analogy to phenyl benzyl sulfoxide.[23] ^{1}H NMR ($CDCl_3$): δ 7.24−7.42 (m, 7 H), 6.97 (dd, J = 1.6, 7.6 Hz, 2 H), 4.10 (d, J = 12.6 Hz, 1 H), 3.98 (d, J = 12.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 63.6, 125.9, 128.5, 128.6, 128.7, 129.2, 130.4, 137.4, 141.3.

Benzyl *p*-methoxyphenyl sulfoxide (8, X = CH_3O) was prepared in analogy to phenyl benzyl sulfoxide.[23] ^{1}H NMR ($CDCl_3$): δ 7.20−7.32 (m, 5 H), 6.89−6.99 (m, 4 H), 4.09 (d, J = 12.3 Hz, 1 H), 3.94 (d, J = 12.3 Hz, 1 H), 3.82 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 55.6, 63.8, 114.4, 126.4, 128.2, 128.5, 129.4, 130.5, 133.7, 162.1.

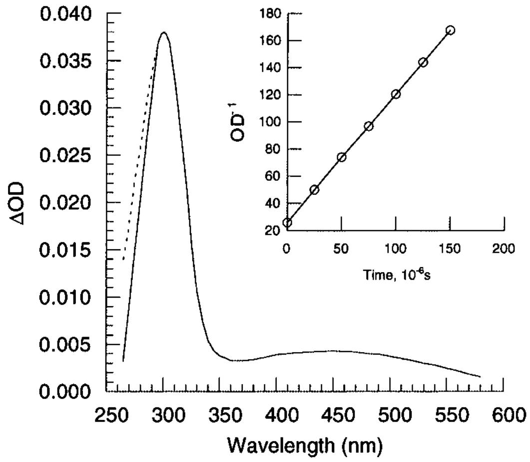
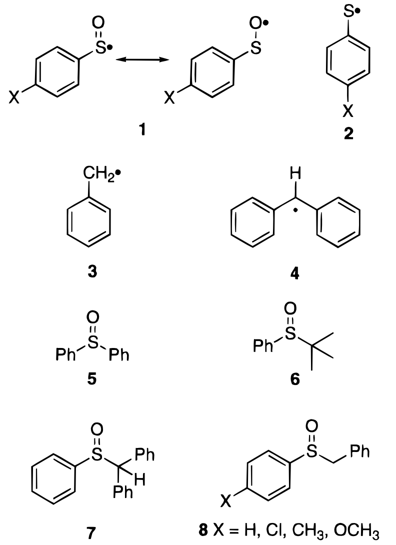


Figure 1. Differential absorption spectrum of PhSO$^•$ radical after excitation of **8** (X = H, 6.2×10^{-5} M) in air-saturated cyclohexane (solid line). Absorption spectrum of PhSO$^•$ corrected for ground state bleaching of sulfoxide (dashed line). Insert: Second order plot of the decay kinetics at 300 nm in the same solution.

CHART 1



Computations. Structural optimizations were carried out using restricted open-shell Hartree−Fock (ROHF) methodology with the GAMESS suite of progams[50] and using unrestricted Hartree−Fock (UHF) and Becke3LYP methodology[51] on the Gaussian 92/DFT suite.[52] Orbitals were visualized with MacMolPlot, which is available as a utility with GAMESS. The default 6-311G basis sets in Gaussian were modified to conform with those in GAMESS, as developed by McLean and Chandler.[53] The use of this basis set only affects sulfur among the atoms used here. Rotational barriers include zero point energies, scaled by a factor of 0.9, and uncorrected for temperature, i.e., at 0 K.

Results

The sulfoxides used in the study are shown in the Chart 1. The excitation of all sulfoxides (**5**−**8**) led to the formation of a transient within the response time of the instrument. A representative example, obtained from compound **8** (X = H) in cyclohexane, is shown in Figure 1. The portion of the transient absorption spectrum with maxima at 300 and 450 nm is not affected significantly by change of the precursor sulfoxide, solvent, or presence of O_2 (e.g., Figure 2). We did not observe any long-lived excited state of the sulfoxide, consistent with our previous assignment of singlet cleavage,[23] but a very short-lived triplet cannot be ruled out.

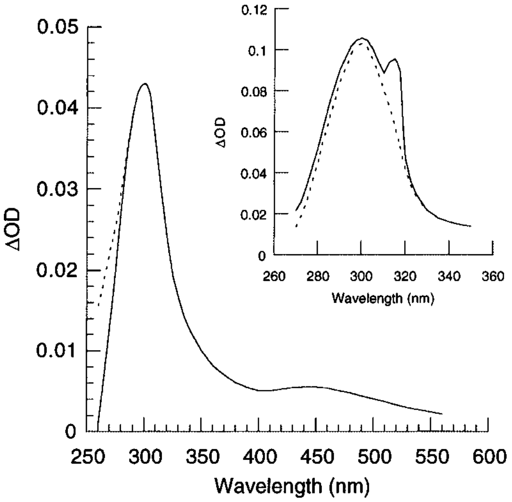


Figure 2. Differential absorption spectrum of PhSO$^\bullet$ after excitation of **8** (X = H, 1×10^{-4} M) in air-saturated 2-methyl-2-propanol (solid line). Absorption spectrum of PhSO$^\bullet$ corrected for the ground state bleaching of sulfoxide (dashed line). Insert: Absorption spectrum of transients after excitation of **8** (X = H, 8.2×10^{-5} M) in degassed acetonitrile immediately after the laser pulse (solid line). Absorption spectrum of PhSO$^\bullet$ only in the same air-saturated solution recorded 200 ns after laser pulse (dashed line).

The decay of the 300 nm transient was very well fit to second order kinetics, and the initial intensity of the signal was directly proportional to the energy of the incident laser pulse. The decay kinetics of the transient and its yield were the same in Ar-flushed, air-saturated, or O$_2$-saturated solutions. For all sulfoxide precursors in acetonitrile (X = H), the signal at λ_{max} = 300 nm decays with the same rate constant: $2k_r/\epsilon = (5.6 \pm 0.3) \times 10^5$ cm s^{-1}. We assigned the transient to the phenylsulfinyl radical **1** (X = H) and the decay kinetics to its self-recombination.

In addition to PhSO$^\bullet$, the excitation of **5** and **6** should lead to the simultaneous formation of phenyl and *tert*-butyl radicals, respectively, with absorption maxima at 260 and 230 nm.[54] However, the low extinction coefficients for these radicals and their peroxy derivatives ($\leq 10^3$ M^{-1} cm^{-1}) imply that those species will not significantly distort the sulfinyl radical signals in deaerated or air-saturated solutions. Because of the strong overlap of these absorption spectra with those of the sulfinyl radical and the starting materials, they could not be recorded. We did observe the absorption of unidentified products at ~320−600 and ~320−350 nm in photolysis of **5** and **6**, respectively. The contributions of these products to the spectra were small, and the lifetimes were ≥ 200 μs in deoxygenated or air-saturated solutions.

Photolysis of benzyl phenyl sulfoxide **8** (X = H) at 266 nm leads to the formation of PhSO$^\bullet$ and benzyl radicals in acetonitrile (Figure 2). The absorption spectrum of benzyl radical has two strong maxima, at 258 and 316 nm.[55−58] It reacts very quickly with O$_2$ and the pseudo-first order lifetime of benzyl in air-saturated acetonitrile should be about 170 ns.[59] Thus, in principle, one could determine the extinction coefficients for absorption by PhSO$^\bullet$ from the data in the insert of Figure 2. In practice this was not possible due to the strong overlap of the two absorption spectra. Additionally, the absorption spectrum of the sulfenic ester formed by geminate recombination of PhCH$_2^\bullet$ and PhSO$^\bullet$ has a maximum at 310 nm, causing further interference.[23,24] Therefore, precursor **7** was chosen for quantitative evaluation of the sulfinyl radical absorption, as the absorption of the diphenylmethyl radical (Ph$_2$CH$^\bullet$) was shifted far enough away to not interfere.

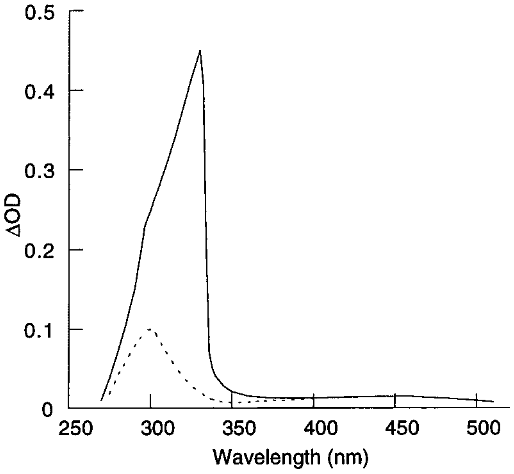


Figure 3. Absorption spectrum of transients after excitation of **4** (6.5×10^{-5} M^{-1} s^{-1}). The solid line is immediately after the laser pulse in Ar-flushed acetonitrile, and the dashed line is for an O$_2$-saturated solution, taken 100 ns after the pulse.

The absorption spectrum of Ph$_2$CH$^\bullet$ is well-known.[56,60−63] It has maxima at 331 and 318 nm (shoulder) with extinction coefficients of 4.4×10^4 and 3.1×10^4 M^{-1} cm^{-1}, respectively.[61] The extinction coefficient at 266 nm is of the order of 3000 M^{-1} cm^{-1}, and it undergoes only photophysical decay processes from excited doublet states.[56,61,63]

Excitation of **7** (at 266 nm) in degassed acetonitrile led to a transient with the clear superposition of Ph$_2$CH$^\bullet$ and PhSO$^\bullet$ absorptions (Figure 3). The decay kinetics of the peak at 331 nm were well-fit by second order decays with $2k_r/\epsilon = 9.3 \times 10^4$ cm s^{-1}. Using Bromberg's estimate of the extinction coefficient, the recombination rate constant of diphenylmethyl was estimated at $2k_r = 4.1 \times 10^9$ M^{-1} s^{-1}. Ph$_2$CH$^\bullet$ reacts effectively with O$_2$.[59,63] Given the concentration of O$_2$ in air-saturated acetonitrile at ambient temperature (1.9 mM)[64] and a first order lifetime of 350 ns, a rate constant for the consumption of benzyl by O$_2$ was roughly estimated at 1.5×10^9 M^{-1} s^{-1}, which compares well with reported values.[63]

Further evidence for the assignment of the transient absorption spectrum in Figure 3 is the observation of fluorescence of Ph$_2$CH$^\bullet$. The radical is created and then excited within the same laser pulse, and an emission spectrum was observed with maxima at 520 and 540 nm, in agreement with observations of other workers.[61−63] Molecular oxygen quenches excited Ph$_2$CH$^\bullet$ even faster than it does the ground state. The observed decay rate of the fluorescence was 3.3×10^6 s^{-1} in Ar-flushed acetonitrile and 2.9×10^7 s^{-1} in air-saturated solution, giving a two-point rate constant of *ca.* 1.5×10^{10} M^{-1} s^{-1}, consistent with the diffusion-controlled quenching rate constant (3.7×10^{10} M^{-1} s^{-1})[65] mitigated by a spin-statistical factor of 1/3 for the reaction[63]

$$\mathrm{Ph_2CH^{\bullet}*} + {}^3\mathrm{O_2} \rightarrow \mathrm{Ph_2CH^{\bullet}} + {}^1\mathrm{O_2}\,({}^1\Delta_g)$$

Because of the rapid quenching of Ph$_2$CH$^{\bullet}$* and Ph$_2$CH$^\bullet$ by molecular oxygen and the relative unreactivity of PhSO$^\bullet$ with oxygen, the transient absorption spectrum observed 100 ns after the laser pulse in O$_2$-saturated solution was strongly dominated by PhSO$^\bullet$ with its characteristic 300 nm λ_{max}. The decay of this transient was second order: $2k_r/\epsilon = 5.4 \times 10^5$ cm^{-1}. Since the concentration of Ph$_2$CH$^\bullet$ and PhSO$^\bullet$ radicals escaped from geminate recombination in the solvent cage should be equal, the extinction coefficient of PhSO$^\bullet$ could be estimated from the spectra at early times and the equation

TABLE 1: Photophysical Properties of the Phenylsulfinyl Radical

solvent	η(25 °C)[a] (cP)	$2k_{r/\epsilon}$ (10^5 cm s^{-1})	$2k_r$[b] (10^9 M^{-1} s^{-1})	k_{dif}(25 °C)[a] (10^9 M^{-1} s^{-1})	$\Phi_{PhSO^\bullet}$
ethyl ether	0.24[c]	12.0	13.0	27	0.18
hexane	0.29	9.0	10.0	22	0.16
acetonitrile	0.34	5.8	6.4	19	0.12
cyclohexane	0.90	5.65	6.2	7.4	0.12
water	0.89	3.6	4.0	7.4	0.10
ethanol	1.08	3.2	3.5	6.1	0.14
1-propanol	1.94	2.3	2.5	3.4	0.12
2-propanol	2.04	2.8	3.1	3.2	0.12
2-methyl-2-propanol	4.31	1.55	1.7	1.5[d]	0.09

[a] At 25 °C.[64,97] [b] These values are estimated from $2k_r/\epsilon$ using $\epsilon_{PhSO^\bullet}$(300 nm) = 1.1 × 10^4 M^{-1} cm^{-1}. [c] At 20 °C. [d] The true value of k_{dif} should be slightly higher due to the addition of 1% water.

$$\frac{\mathrm{OD}_{\mathrm{PhSO}^\bullet}(300\ \mathrm{nm})}{\varepsilon_{\mathrm{PhSO}^\bullet}(300\ \mathrm{nm}) - \varepsilon_o} = \frac{\mathrm{OD}_{\mathrm{Ph2CH}^\bullet}(331\ \mathrm{nm})}{\varepsilon_{\mathrm{Ph2CH}^\bullet}(331\ \mathrm{nm})}$$

where $\epsilon_0 = 5 \times 10^2$ M^{-1} cm^{-1} and is the extinction coefficient of the ground state of sulfoxide at 300 nm. The dependences of the yield of both radicals on the energy of the laser pulse were strictly linear. From data presented in Figure 3, we obtained $\epsilon_{PhSO^\bullet}(300\ \mathrm{nm}) = (1.1 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}.

As measured by this technique, the extinction coefficient of PhSO$^\bullet$ is practically independent of solvent. Thus, the quantum yield of PhSO$^\bullet$ avoiding geminate recombination and escaping into the bulk ($\Phi_{PhSO^\bullet}$) in different solvents can be easily estimated. The yield of PhSO$^\bullet$ was measured in comparison with the triplet−triplet absorption of anthracene in degassed cyclohexane with these parameters: $\Phi_T = 0.71$ and ϵ_T(422.5 nm) = 6.47 × 10^4 M^{-1} cm^{-1}.[66−68] The optical density at the excitation wavelength and the energy of laser pulse (7 mJ) were equal for solution of sulfoxide and anthracene. These data, together with the decay rate constants, are presented in Table 1. The $\Phi_{PhSO^\bullet}$ values for the different sulfinyl precursors are shown in Table 2.

Reactions with Nitroxides. Rate constants for reactions of sulfinyl radicals with stable nitroxide radicals were determined and compared with the corresponding rate constants for PhS$^\bullet$ from the literature. Both TEMPO and DTBN were used. Rate constants were found by the usual first order expression

$$k_{obs} = k_0 + k_{rxn}[\mathrm{NO}^\bullet]$$

and are shown in Table 3. The values obtained for PhS$^\bullet$ (*vide infra*) are in good agreement with previous accounts.[45]

It is known that the photolysis of DTBN goes by way of C−N homolytic cleavage with formation of 2-methyl-2-nitrosopropane and the *tert*-butyl radical (which is quickly trapped by another mole of nitroxide).[69] By contrast, TEMPO is known to be an efficient hydrogen abstractor.[70] In principle, such radical intermediates themselves or the decomposition products therefrom could interact with the sulfur-centered radicals under investigation, especially at higher nitroxide concentrations. However, the dependence of the sulfinyl radical decay rates on the nitroxide concentration was linear and independent of laser pulse energy, and such potential problems were neglected. Direct excitation of the nitroxides in the absence of sulfoxides did not result in observation of any transients from 260 to 600 nm.

A similar experiment was carried out with galvinoxyl in acetonitrile. Only an upper limit for the rate constant of interaction between PhS$^\bullet$ and PhSO$^\bullet$ radicals with galvinoxyl ($k \leq 1 \times 10^9$ M^{-1} s^{-1}) could be established because the galvinoxyl was destroyed by the laser pulse.

TABLE 2: Quantum Yields of Sulfinyl Radicals and Consumption of Sulfoxides

sulfoxide	solvent	$\Phi_{PhSO^\bullet}$	Φ_{chem}[a]
PhSOPh (**5**)	cyclohexane	0.06	
	2-methyl-2-propanol	0.05	0.034
PhSOC(CH$_3$)$_3$ (**6**)	cyclohexane	0.12	
PhSOCHPh$_2$ (**7**)	acetonitrile	0.18	
PhSOCH$_2$Ph (**8**)	cyclohexane	0.11	
	2-methyl-2-propanol	0.09	0.20

[a] The quantum yield for chemical consumption of the sulfoxide.[23,24]

TABLE 3: Rate Constants for Reaction of PhS$^\bullet$ and PhSO$^\bullet$ with Stable Radicals

radical	σ^+	λ_{max} (nm)	k_{rxn} (10^8 M^{-1} s^{-1}) TEMPO	DTBN	solvent
1 (X = Cl)	0.11	310, ∼460	15.6	14.4	acetonitrile
1 (X = H)	0	300, 450	9.4	10.0	acetonitrile
1 (X = CH$_3$)	−0.31	310[b]	8.4	9.7	acetonitrile
1 (X = OCH$_3$)	−0.78	320, 515[c]	7.8	8.1	acetonitrile
1 (X = Cl)	0.11	310, ∼460		32	hexane
1 (X = H)	0	300, 450		29	hexane
1 (X = CH$_3$)	−0.31	310[b]		23	hexane
1 (X = OCH$_3$)	−0.78	320, 515		23	hexane
1 (X = CH$_3$)	−0.31	310[b]		13	cyclohexane
2 (X = Cl)	0.11			16[a]	cyclohexane
2 (X = H)	0	295	14	17	acetonitrile
2 (X = H)	0	295		13[a]	cyclohexane
2 (X = CH$_3$)	−0.31			7.5[a]	cyclohexane
2 (X = OCH$_3$)	−0.78			3.3[a]	cyclohexane

[a] Reference 45. [b] Very small absorbance about 450 nm. [c] Ratio of maxima in differential absorption spectrum is 2.8:1.

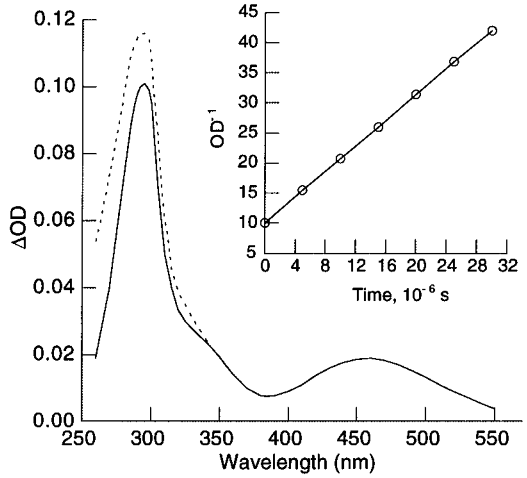


Figure 4. Differential absorption spectrum of PhS$^\bullet$ after excitation of PhSSPh (5.5 × 10^{-5} M) in air-saturated acetonitrile (solid line). Absorption spectrum of PhS$^\bullet$ corrected for ground state bleaching of sulfide. Insert: Second order plot of the decay kinetics at 295 nm.

Phenylsulfenyl Radicals. Phenylsulfenyl radicals (PhS$^\bullet$) were produced by the direct photolysis of diphenyl disulfide. In relatively inert solvents, the only significant decay pathway is recombination, both geminate and random.[42,45,47] The absorption spectrum of PhS$^\bullet$ varied with solvent (Figures 4 and 5) but was characterized by maxima at about 295 and 460 nm. The microsecond-domain kinetics were strictly second order, and neither the initial intensity nor the decay kinetics depended on the presence of O$_2$.

Assuming that the oscillator strength *f* is proportional to $n(n^2 + 2)^{-2}\int\epsilon\ d\nu$ (where *n* is the refractive index of the solvent) and is a constant in various solvents,[71] ϵ values for PhS$^\bullet$ were obtained from the current data and previous reports from aqueous solution.[43] They are reported in Table 4. Also

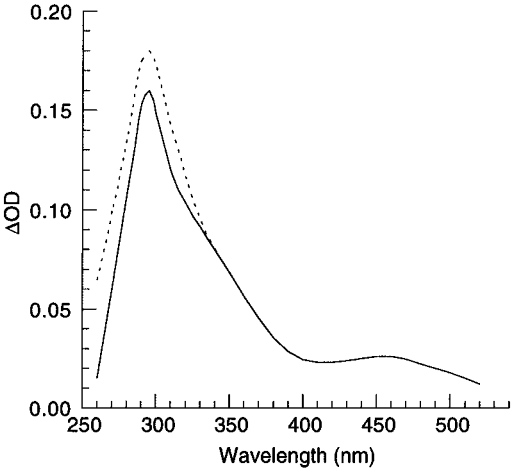


Figure 5. Differential absorption spectrum of PhS• after excitation of PhSSPh in air-saturated 2-propanol (solid line). The dashed-line spectrum is corrected for bleaching of ground state PhSSPh.

TABLE 4: Photophysical Properties of the Phenylsulfenyl Radical (PhS•)

solvent	$2k_{r/\epsilon}$ (10^5 cm s^{-1})	ϵ(295nm) (10^4 M^{-1} cm^{-1})	$2k_r$ (10^9 M^{-1} s^{-1})	k_{dif}(25 °C)[64] (10^9 M^{-1} s^{-1})	$\Phi_{PhS^\bullet}$
acetonitrile	11.0	0.70	7.7	19	1.1
cyclohexane	6.5	0.90	5.9	7.4	1.3
2-propanol	4.8	0.67	3.2	3.2	1.2
2-methyl-2-propanol	2.7	0.67	1.8	1.5[a]	0.85

[a] The actual value may be slightly higher since 1% water was added to the solvent.

estimated were recombination rate constants and quantum yields of PhS• radicals in the bulk solvent ($\Phi_{PhS^\bullet}$). It is worthwhile to note that the quantum yield of disulfide decomposition and escape leading to formation of two fully separated PhS• radicals in solvent equals $\Phi_{PhS^\bullet}/2$. Also, while the self-termination rate constants $2k_r$ are essentially identical for PhS• and PhSO•, the $\Phi_{PhS^\bullet}$ values are much larger than those of $\Phi_{PhSO^\bullet}$.

Computations. In order to further characterize the sulfinyl radicals, computations were carried out to determine the character of the singly-occupied molecular orbital (SOMO) of PhSO•. An extensive computational project regarding smaller sulfinyl radicals and related species will be published elsewhere.[72] Both HSO• and $CH_3SO^\bullet$ are of C_s symmetry. In principle, the ground state could be either $^2A'$ or $^2A''$, corresponding to a σ-type or π-type singly occupied orbital. Our CASSCF calculations on these species showed both ground states to be of A″ symmetry, consistent with previous theoretical[28,73,74] and experimental[26,75,76] determinations on HSO•. ROHF calculations also give a $^2A''$ ground state in all cases, and the singly occupied orbitals obtained from the CASSCF calculations on the smaller systems were very similar to those from ROHF. Thus, MCSCF calculations were not carried out on PhSO• when less expensive methods were expected to give qualitatively similar results.

Three general conformations of PhSO• were considered: a $C1$ conformation, where the CSO plane is rotated to an arbitrary degree relative to the phenyl plane, and two limiting C_s conformations with the CSO plane parallel and perpendicular to the phenyl plane. No stationary points were found that were not essentially C_s in symmetry. (Shallow potentials allowed the structure to "optimize" without coming to the exact 0 or 90° dihedral angle.) The geometry with the CSO plane at a 90° dihedral angle was found to be a transition state with a single imaginary vibrational frequency whose vectors involved rotation of the C−S bond. The planar form was a true minimum at all computational levels.

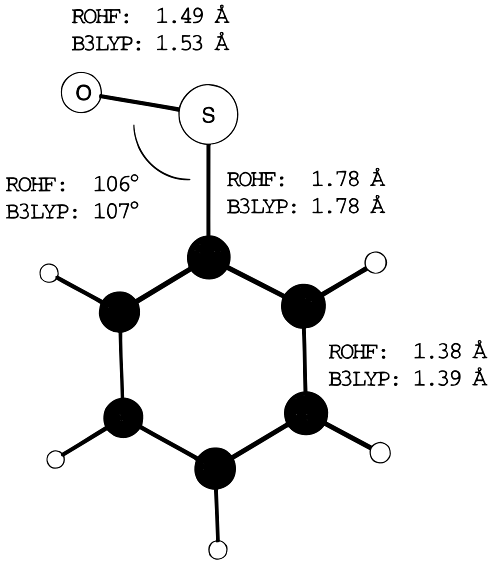


Figure 6. Computed geometry for PhSO•. Values in parentheses are from Becke3LYP/6-31G+(d,p) calculations, and others are from ROHF/6-31G+(d).

Preliminary calculations on PhSO• were carried out at the UHF/3-21G(d) level. These served as useful starting geometries for other calculations. However, it was evident that the UHF model would not be appropriate given the significant spin contamination obvious from an S^2 value of 1.31. (When the phenyl group was substituted with a non-conjugating group such as CH_3, the spin contamination was much less.) Subsequent ab initio calculations were done with the ROHF method, and energies were reevaluated with single point calculations with second order Møller−Plesset perturbation theory, truncated at the second order (RMP2).[77] The Becke3LYP hybrid density functional was also used to optimize structures. Single point energies were obtained with a larger basis set, as indicated below.

The optimized geometry for PhSO• at ROHF/6-31+G(d) is shown in Figure 6, and several computed quantities are given in Table 5. Including zero point energies, the barrier to rotation (i.e., the difference in energy between this conformation and the transition state with a 90° dihedral angle) is 2 kcal/mol. With the RMP2 electron correlation correction, this barrier rises to 13 kcal/mol. The computed singly occupied molecular orbital is essentially a π^* S−O orbital, with minor delocalization (ca. 1%) on the ortho and para carbon atoms. Mulliken analysis of the SOMO showed a 48% contribution from S p-orbitals and a nearly identical 48% contribution from the O p-orbitals. Similarly, Mulliken analysis places a +0.55 charge on the sulfur and −0.52 on the oxygen. Interestingly, although the delocalization of the SOMO into the phenyl ring is minimal, conjugation apparently draws spin density onto the sulfur atom, at least at the ROHF level; the 90° transition state showed a 76% contribution from the O atom and 24% from S. Mulliken charges on S and O and the bond order are all slightly lower at the transition state. A surprisingly large S−O bond lengthening (0.06 Å) for the transition state is also observed at the ROHF level.

Using the Becke3LYP hybrid density functional method, the structures were optimized with the 6-31+G(d,p) basis set, and single point energies were done with the 6-311+G(3df,2p) basis set. This basis set was chosen because of results with other, smaller sulfinyl radicals that indicated it was necessary for good energies.[72] The calculated rotational barriers are effectively

TABLE 5: Computed Parameters for $PhSO^{\bullet}$

quantity	ROHF/ 6-31+G(d)	MP2/6-31+G(d)// ROHF/6-31+G(d)	Becke3LYP/ -31G+(d,p)	Becke3LYP/6-311G+(3df,2p)// Becke3LYP/6-31G+(d,p)
S−O bond length (Å)	1.49		1.53	
spin density, S[a]	0.48		0.49	0.52
spin density, O[a]	0.48		0.41	0.39
rotational barrier (kcal/mol)	2.0	13.0	4.4	5.0
S−O bond length (transition state) (Å)	1.55		1.54	
spin density, S[a] (transtion state)	0.23		0.49	0.54
spin density, O[a] (transition state)	0.76		0.48	0.46

[a] Mulliken approximation.

identical for the two basis sets with Becke3LYP—about 5 kcal/mol. The Becke3LYP calculations show a S−O bond length which varies much less with C−S bond rotation than in the ROHF calculations but is much larger in the ground state structure than for the ROHF calculation.

Like the ROHF calculations, Becke3LYP places the unpaired electron in an orbital that is essentially S−O π^*. The planar structure has some delocalization ($\leq$10%) onto the ortho and para positions on the ring, but this delocalization is severely limited in the transition state, where the S−O π^* orbital has no overlap with the phenyl π system.

Because of the disagreement between S−O bond lengths obtained at ROHF/6-31+G(d) and those at Becke3LYP/6-31+G(d,p) (1.49 Å *vs* 1.53 Å), the planar structure was also optimized at other levels. Several basis sets were examined with the ROHF model. Moving from double-ζ to triple-ζ had no significant effect; neither did adding p functions to the hydrogens or removing the diffuse functions. However, there was some variation with the number of d polarization functions. With one, two, or three d functions on the heavy atoms, the S−O bond length was found to be 1.49, 1.47, and 1.49 Å, respectively. Using the BLYP functional (*vide infra*) and the 6-31+G(d,p) basis set, an S−O bond length of 1.55 Å was obtained.[78,79]

Discussion

Role of Sulfinyl Radicals in Sulfoxide Photochemistry. This work represents the strongest and most direct evidence for the intermediacy of sulfinyl radicals in sulfoxide photochemistry, as outlined in Scheme 1. The observation of the same transient from precursors **5**−**8** and in the variety of solvents leaves little doubt of the assignment of the transient illustrated in Figure 1.

Typically, sulfenic esters that are formed by sulfoxide photolysis undergo secondary photolysis to give sulfenyl/alkoxyl radical pairs.[13,23,80−84] In principle, then, a single intense laser pulse could carry out two sequential photochemical reactions, generating a sulfenyl radical for spectroscopic observations. While we cannot rule out this occurrence to a minor extent, the distinct spectral characteristics of the $PhSO^{\bullet}$ and $PhS^{\bullet}$ radicals and the linear dependence of the signal strengths on laser pulse energy seem to rule it out as a major problem with these experiments. Only in the fluorescence of $Ph_2CH^{\bullet}$ do we see evidence of a two photon process of any sort.

The current data are consistent with our previous steady state results. For instance, from ref 23, it can be derived that the quantum yield of $PhSSO_2Ph$ (the ultimate dimerization product of $PhSO^{\bullet}$) from photolysis of **8** (X = H) is about 0.055. In Table 1, the quantum yield of free $PhSO^{\bullet}$ is shown as 0.12. Given a pure second order decay of the free $PhSO^{\bullet}$, a thiosulfonate quantum yield is predicted as 0.06. Since these numbers are arrived at quite independently, their consistency serves as a good check on the extinction coefficient value determined for $PhSO^{\bullet}$.

Among the compounds tested, the maximum quantum yield of free $PhSO^{\bullet}$ radical production is observed for phenyl diphenylmethyl sulfoxide, **7** (Table 2). Because of the time scale of the experiment, the value of $\Phi_{PhSO^{\bullet}}$ is actually Φ_{cleave} times the fraction of radical pairs which escape the geminate cage without some kind of reaction. The structural features of **4** are consistent with both favorable cleavage and steric hindrance to recombination, and we are unable to separate these aspects from the data quantitatively. However, the trend of values of $\Phi_{PhSO^{\bullet}}$ as a function of precursor is clearly in order with expectations.

There is also the matter of the value of $\Phi_{PhSO^{\bullet}}$ as a function of solvent (Table 1). Over a little more than 1 order of magnitude variation in viscosity, the quantum yield drops by about a factor of 2. The simplest notion correlating free radical quantum yields and viscosity from a solvent continuum model predicts that $\Phi_{R^{\bullet}}$ should monotonically approach zero with increasing η. However, this model neglects important specific solvent−solute interactions.[85] Given the computational results that put a significant negative charge on the oxygen of the sulfinyl radicals, it is likely, for instance, that they are solvated much better by alcohols than by alkanes. It is thus interesting to note that $\Phi_{PhSO^{\bullet}}$ values are very similar in all of the solvents, save the least viscous (η < 0.3 cP, higher $\Phi_{PhSO^{\bullet}}$) and most viscous (η > 4 cP, lower $\Phi_{PhSO^{\bullet}}$), especially noting that the more viscous solvents within the middle group are alcohols. Specific solvation would be expected to increase the $\Phi_{PhSO^{\bullet}}$.

Computational Characterization of $PhSO^{\bullet}$. Previous workers have described $PhS^{\bullet}$ as having its spin essentially localized on the S atom on a p-type orbital, with a single bond between the carbon and sulfur.[47] In a sense, the computational results for $PhSO^{\bullet}$ are similar. Fundamentally, we find that the unpaired spin lies almost entirely outside the ring in a π^* orbital constructed almost entirely of S and O p-orbitals (Table 5). Only a trivial delocalization of the spin is observed into the phenyl ring.

It has long been known that inclusion of polarization functions in the basis set is necessary for accurate calculations of the properties of hypervalent sulfur compounds such as sulfoxides.[86] Given the results at the various basis sets, we believe 1.49 Å is the best estimate of the ROHF value of the S-O bond length. Experimental and computed bond lengths of typical sulfoxides are 1.48−1.49 Å.[87]

Significant variation is observed between the ROHF, Becke3LYP, and BLYP S-O bond lengths for $PhSO^{\bullet}$ (Figure 6 and BLYP/6-31+G(d,p) = 1.55 Å). Comparison with the work of Cramer and co-workers may shed light on this issue. They carried out a series of computational studies on phosphorus-containing radicals, some of which have considerable structural analogy to the present sulfinyl radicals (*e.g.*, $Me_2PO^{\bullet}$).[88,89] Using the 6-31G(d,p) basis set, they found that UHF geometries are more reliable than BLYP and other density functionals for predicting hyperfine coupling constants, with the latter producing P−X bonds longer than other methods by 0.02−0.06 Å. Even the hyperfine coupling constants calculated with Becke3LYP were more accurate when done at the UHF geometry, though the difference is not as large as with other density functional methods. Using this experience as a guide, one may suggest that the 1.53 Å value is an upper limit, and the true length may be closer to 1.49 Å, that is, about the same as, or a little longer than, that of the sulfoxide.

In a previous computational work on sulfoxides in which S−O bond dissociation energies were determined by isodesmic exchange of the oxygen between a test sulfoxide and dimethyl sulfide, it was found that certain structural features led to significant differences in computed bond energies between Hartree−Fock and Møller−Plesset methods.[87] Moreover, Hartree−Fock methods are not generally reliable for predicting transition state energies. Therefore, it is not surprising to see a significant difference in the rotational barriers for PhSO• calculated by ROHF and RMP2 methods, though the magnitude of difference (2 kcal/mol *vs* 13 kcal/mol) is large in this case. The Becke3LYP data (*ca.* 5 kcal/mol) are intermediate. One may speculate that very likely the ROHF number is too low, and the true value may lie between the density functional and ROMP2 results.

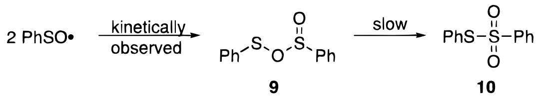
Intermolecular Reactivity of Sulfinyl Radicals. There are three types of reactions reported here for sulfinyl radicals: that with O_2, that with themselves, and that with nitroxides. We begin with the reaction with O_2. An upper limit of approximately 10^7 M^{-1} s^{-1} can be estimated for the apparent rate constant for the reaction of O_2 and PhSO•. We make no claim that PhSO• is "inert" to O_2, merely that it is effectively so under these conditions because of the limited lifetime due to self-termination. Furthermore, a rapidly reversible reaction between PhSO• and O_2 is also consistent with our data.

The self-termination reaction of PhSO•, however, is interesting for its speed, rather than the lack thereof. Previous to this work, two reports of sulfinyl radical self-termination reactions were available; both used kinetic EPR to determine rate constants at low temperature. The *tert*-butylsulfinyl radical dimerizes with rate constant $2k_r = 6 \times 10^7$ M^{-1} s^{-1} at −100 °C.[90] More directly comparable, **1** (X = Cl) and its 2,5-dichloro analog were studied over a temperature range of about 185−250 K in toluene.[91] The activation energy of the dimerization reaction (1.7 and 2.4 kcal/mol) is consistent with a diffusion controlled process. The rate constants $2k_r$ extrapolate up to 2×10^9 and 1×10^9 M^{-1} s^{-1} at 298 K, respectively, in quite reasonable agreement with the current results, particularly given the extrapolation.

The results presented in Tables 1 and 4 show that an increase in solvent viscosity leads to a decrease of the recombination rate constant ($2k_r$) of the sulfur-centered radicals. In 2-propanol and 2-methyl-2-propanol $2k_r = k_{dif}$, where k_{dif} is the diffusion controlled rate constant. None of the $2k_r$ values dip below 0.33 k_{dif}. For radicals without steric hindrance and a low value of spin−orbital coupling, $2k_r$ should be $0.25k_{dif}$ because of the spin statistical effect of doublet recombination.[92] Our results thus point out that there is a significant spin−orbit coupling in radical pairs of both types (sulfenyl and sulfinyl) of sulfur-centered radicals investigated. Previous workers, who observed a lack of magnetic field effects for the ArS• radical pairs in micelles, came to similar conclusions for that radical.[46]

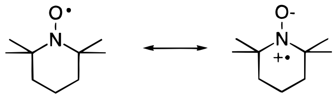
Our inclusion of data for PhS• is mainly for comparison to PhSO•. Our estimates of the extinction coefficients for the absorption spectra in various solvents depend on the previous assignment of the spectrum in water.[43] However, since the rate constants depend on the chosen value of ϵ, their proper magnitude (given the expectations for spin−orbit coupling from previous results) and similarity to the PhSO• values lend confidence to the assignment.

The nature of the initial structure formed by sulfinyl dimerization is not known for certain, but it has been assumed that it is the mixed sulfenic-sulfinic anhydride **9**, as opposed to the O−O or S−S bonded dimers.[34,54] Whatever the initial structure, the isolated structure for sulfinyl dimerization is a thiosulfonate, in this case **10**. There clearly is a second rearrangement which occurs to generate these compounds. As alluded to previously, steady state photolysis of **7** leads to product mixtures which contain the appropriate thiosulfonate, particularly in less viscous solvents.[23,24]



Finally, we return to the reactions of ArSO• with other molecules. Using steady state experiments and *E*/*Z* isomerization of alkenes as a probe, previous workers have suggested that sulfinyl radicals add reversibly to alkenes, but we are aware of precious little other data regarding sulfinyl reactivity in solution.[34,93]

We have obtained the first absolute rate constants for reactions of sulfinyl radicals with other molecules, as reported in Table 3. Unlike the self-termination reactions, these reactions, while fast (*ca.* 10^9 M^{-1} s^{-1}), are dinstinctly below the diffusion controlled rate constant, and the rate constants do not vary much with the range of substituents shown in the table. The nitroxides are expected to behave as electron rich radicals, as illustrated by the following resonance structures and by the well-known increase of the nitrogen hyperfine coupling constant with solvent polarity.



PhS•, in its reactions both with nitroxides and with olefins,[44] exhibits a polarity effect consistent with an electron poor reactivity. This trend is evident in Table 3 for the different substituents of **2**. Whereas there is a range of about a factor of 4 over the sulfenyl series from X = Cl to OCH_3, the trend, while in the same direction, is less than a factor of 2 in either polar or nonpolar solvents for the sulfinyl series. Presumably this is due to the presence of the negatively charged oxygen atom; it can be speculated that the charge on S and O is dominated by their mutual interaction and that the perturbation by the remote substitutions is smaller.

It is interesting to note that the rate constants for reactions of nitroxides with ArS• and ArSO• radicals, though below diffusion control, are higher than any of the published values for similar sized carbon centered radicals.[94] Benzyl, for instance, is trapped by TEMPO with a rate constant of 9.5×10^7 M^{-1} s^{-1} in acetonitrile (at 18 °C), about an order of magnitude more slowly than in PhSO•.[95] This difference is contributed to by both electronic structure and steric hindrance. We presume that the effect is not entirely steric, since the rate constant for radical trapping by TEMPO decreases only by a factor of 4 from the benzyl to the cumyl radical.

Although we did not attempt to isolate any products, we assume the reaction of sulfinyls and nitroxides certainly proceeds by coupling between the O atom of the nitroxide to the S and/or O of the sulfinyl radical. This leads to an analogy between the nitroxide and sulfinyl structures that may be useful in supporting the presumed mode of sulfinyl dimerization.

The nitroxides are at least qualitatively isolobal with the sulfinyl radicals (see resonance structures above), and the unpaired spin is expected to reside in an N−O π^* orbital.[96] Preliminary calculations confirm this. However, nitroxides can only react at the partially negative oxygen center for energetic and steric reasons. Therefore, the coupling between the nitroxide and the sulfinyl can be seen as a model for the sulfinyl self-termination reaction in which one of the sulfinyls is constrained to react at its O atom. Given that the rate constants for sulfinyl−nitroxide reaction are within less than an order of magnitude of the dimerization rate constants (and considering the steric bulk of the nitroxide) and the comparable dipole relationship of the N−O and S−O bonds, we suggest that these data support the mode of reaction shown above.

Summary

The transient absorption spectrum of arylsulfinyl radicals has been observed, confirming with direct evidence the photochemical pathway of α-cleavage for aromatic sulfoxides. A determination of extinction coefficients for the parent phenylsulfinyl radical was made. It was found that, though kinetically unreactive to molecular oxygen, the sulfinyl radical self-quenches with rate constants quite closely approaching the diffusion controlled limit, implying that large spin−orbit couplings overcome typical spin-statistical concerns. Reactivity with nitroxide radicals is very high but is not as variable as that of corresponding arenesulfenyl radicals when substituted in the para position. Computational studies indicate that the singly occupied orbital is largely localized on S and O in a π^* configuration lying most heavily on O.

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