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Photochemistry of Benzyl β-Naphthyl Sulfoxide and Characterization of the β-Naphthylsulfinyl Radical[1]

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Abstract. Photolysis of benzyl β-naphthyl sulfoxide results mainly in α-cleavage. The isomeric sulfenic ester is the major product. Because the triplet energies of both the sulfoxide and sulfenic ester are below that of acetone, in contrast to the previously studied phenyl and tolyl cases, interpretation of sensitization experiments is straightforward. The sulfinyl radical is characterized by transient absorption and a model is proposed to account for its reactivity with nitroxide radicals. © 1997 Elsevier Science Ltd.

The photochemistry of several phenyl and tolyl alkyl sulfoxides has been shown to proceed by way of homolytic cleavage of the alkyl-sulfur bond.[2-4] At higher conversion, isolated products are due to secondary photolysis of the sulfenic ester which is formed in the first photochemical reaction. However, a disadvantage of these phenyl and tolyl sulfoxides is that they absorb light only at relatively high energies. Moreover, a significant mechanistic question remained regarding their acetone-sensitized photolysis. Though typical products of sulfenic ester decomposition were observed, benzyl benzenesulfenate was never observed during acetone-sensitized photolysis of benzyl phenyl sulfoxide. It was postulated that this was due to the triplet energy of benzyl phenyl sulfoxide being slightly larger than that of acetone while that of the sulfenic ester was below. This would allow for selective sensitization of the sulfenic ester, even at low conversion.

We now report the photolysis of benzyl β-naphthyl sulfoxide (**1**), whose absorption extends beyond 325 nm and whose triplet energy is below that of acetone and many other triplet sensitizers. Though the chemistry follows a pattern similar to previous examples, we report for the first time observation of the sulfenic ester under triplet-sensitized conditions. We also characterize the β-naphthylsulfinyl radical by flash photolysis and point out an interesting structural analogy between sulfinyl and nitroxyl radicals that leads to an appreciable solvent effect on reaction rate constants.

Steady State Photolyses. The luminescence of several aromatic sulfoxides has previously been reported to be weak, and that of **1** is no exception.[5] The fluorescence and phosphorescence could be recorded at 77 K in EtOH/MeOH glass. A singlet energy of 89 kcal/mol and a triplet energy of 61 kcal/mol were obtained, with a phosphorescence quantum yield of 0.050 ± 0.005.[6]

The photolysis of **1** to high conversion gives a complex reaction mixture. However, photolysis of **1** to modest conversion allows analysis of the primary and secondary products. Argon flushed solutions of **1** (3 mM) in CH_3CN were photolyzed at 267 ± 12 nm using a 150 Xe lamp filtered through a monochrometer. Relative product distributions at approximately 15% conversion are shown in Table 1. The quantum yield for all chemical processes of **1** under these conditions was found to be 0.12. Mass balances are about 85% and equal for the napthyl and benzyl portions of the substrate. To separate primary and secondary photolysis products, the mixture was analyzed by HPLC every few minutes.[7] Proposed pathways and data from a typical single run are shown in Figures 1 and 2.

Table 1. Relative product distributions from **1** in direct and sensitized photolyses at *ca.* 15% conversion.

	4	**7**	**8**	**9**	**10**	**11**	**12**	**13**	$ArSO_nH$
CH_3CN (direct)	60	2	16	4	5	5	-	-	8
acetone (sensitized)	15	4	8	3	5	-	24	31	10

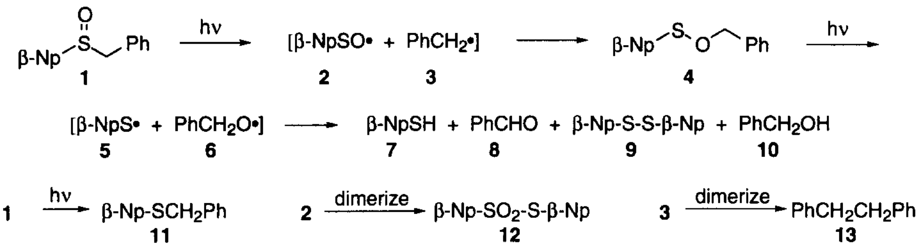


Figure 1. Pathways of product formation

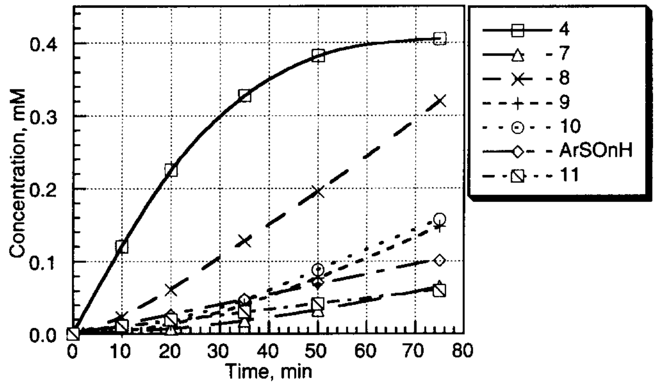


Figure 2. Photolysis products of **1** as a function of time

The predominant primary photochemical product on direct irradiation is the sulfenic ester **4** ; neither of the "escape" products from the pimary radical pair (*i.e.*, **12** and **13**) were observed. Most of the other products derive from secondary photolysis of **4**. Upward curvature in the data for the products **7** - **10** show that they are secondary products. This was confirmed by shifting the wavelength of excitation from 267 to 294 nm, where **4** has a larger extinction coefficient than **1**. Under those conditions, the peak concentration of **4** was lower and occured earlier (at approximately 12 minutes), and the grow-in of products **7** - **10** was also faster.

The production of sulfide **11** was quite linear over the first 80 minutes and is assigned to a 1-photon process. Photochemical deoxygenation of some more complex naphthyl sulfoxides has been observed previously.[8] We have presented evidence that at least some deoxygenations occur by direct S-O cleavage, and the singlet energy of **1** is compatible with this mechanism.[9]

The production of β-naphthalenesulfinic and β-naphthalenesulfonic acids was also observed. Although their UV spectra differ slightly, these two acids were difficult to separate by HPLC, and are therefore listed as a single peak. The mechanism for their formation is not clear, but they may originate from trapping of **2** with adventitious O_2. Once the sulfinic acid is formed, thermal disproportionation is a pathway to the sulfonic acid.[10]

Repetition of these photolyses at 300 nm in the presence of various concentrations of isoprene (as a triplet quencher) showed that at least 90% of the total decomposition of **1** was unquenched. A small fraction of **1*** may undergo intersystem crossing to the triplet before α-cleavage and be vulnerable to quenching.

Acetone sensitization (E_T ~ 79 kcal/mol) led to a dramatically different product distribution that is consistent with triplet chemistry. At 15% conversion in acetone, the major products are the "escape" dimers **12** and **13**. The sulfide is not found, consistent with the hypothesis that this is a singlet chemistry product. Most important, however, is the observation of sulfenic ester **4**. In our previous work with benzyl phenyl sulfoxide, the analogous sulfenic ester was never observed under acetone sensitization. The present results strengthen the contention that acetone sensitization of simple phenyl alkyl sulfoxides proceeds through

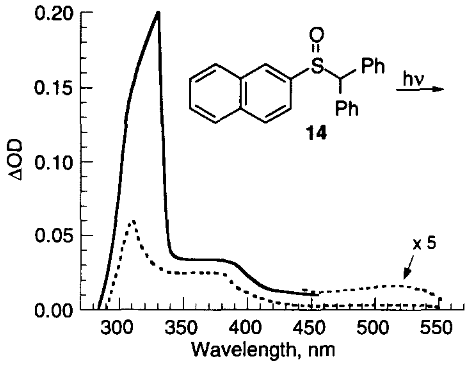


Figure 3. Transient absorption spectra

straightforward triplet sensitization, even though the triplet energy of such sulfoxides are probably a few kcal/mol higher than that of acetone.

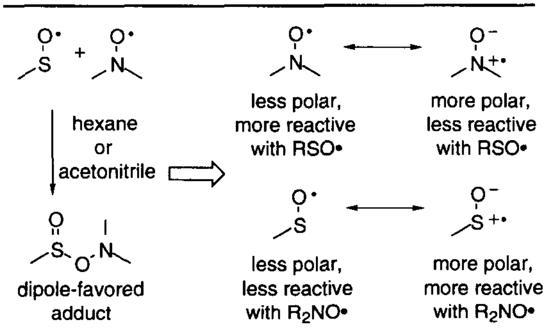
Flash Photolyses.[4] Flash photolysis of sulfoxide **14**[5] at 266 nm leads to formation of the transient whose spectrum is shown as the solid line in Figure 2. The maximum at 331 nm is assigned to diphenylmethyl radical ($Ph_2CH\bullet$).[11,12] Its decay was purely second order. However, in O_2-saturated CH_3CN, its lifetime is about 70 ns. The dotted lines in Figure 2 are the transient absorption spectra obtained 100 ns after the laser pulse under these conditions. The transient is well fit to second order decay ($2k_r/\varepsilon = 2.8 \times 10^5$ cm s^{-1}) under O_2 saturation, indicating that it has a rate constant for reaction with O_2 that is $\leq 1 \times 10^7$ $M^{-1}s^{-1}$. An identical 310 nm transient is observed 200 ns after the laser pulse for solutions of **1** in O_2-saturated CH_3CN . This signal is assigned to the sulfinyl radical **2** based on the observed steady state chemistry and on precedent from the phenyl alkyl sulfoxides.[4] The extinction coefficient (at λ_{max}) for **2** was estimated to be 1.3×10^4 $M^{-1}cm^{-1}$.[4] This leads to second order decay rate constants $2k_r$ of 3.6 and 5.1×10^9 $M^{-1}s^{-1}$ in acetonitrile and hexane, respectively. Quantum yields of 0.17 were determined for formation of **2** from both precursors. The self-quenching rate constant $2k_r$ of **2** was determined over a range of 0 - 60 °C, and an activation energy of 0.2 ± 0.1 kcal/mol was obtained.

Reaction rate constants for **2** with the stable nitroxyl radicals 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and di-*tert*-butyl nitroxyl (DTBN) are shown in Table 2. Activation parameters measured over a temperature range of 0 - 60 °C are shown in Table 2. They compare favorably with previous data for nonyl and benzyl radical trapping by TEMPO.[13] The activation energies are all ≤ 2.2 kcal/mol, suggesting that the constraint of the rate constants below diffusion control is entropic in origin.[14] Beckwith suggested the sub-diffusion controlled rates for carbon-centered radical trapping by nitroxides are due to the loss of entropy inherent in localizing the unpaired electron on the oxygen of the nitroxide.[15]

Table 2. Nitroxyl quenching of β-NpSO•

Nitroxyl	Solvent	k (23 °C), 10^9 $M^{-1}s^{-1}$	E_a, kcal/mol	log A
TEMPO	CH_3CN	1.1	0.65 ± 0.1	9.5
	hexane	2.2	1.6 ± 0.2	10.5
DTBN	CH_3CN	1.2	0.7 ± 0.2	9.6
	hexane	2.7	2.2 ± 0.2	11.0

The rate constant for quenching of $PhCH_2\bullet$ by TEMPO falls by a factor of 5 on going from hexane to acetonitrile.[15] This was attributed to decreased spin density on the O atom in polar solvents, as indicated by hyperfine coupling constants. The solvent effect on rate constants is much smaller for sulfinyl couplings with nitroxyls. This can be qualitatively explained by examination of the solvent effect on the sulfinyl radical electronic structure. Application of a self-consistent reaction field model (*i.e.*, a dielectric continuum "solvent")[16] to ROHF/6-31G(d,p) optimized structures of PhSO• and $(CH_3)_2NO\bullet$ led to similar increases in Mulliken spin densities on O



at the expense of S and N, respectively, on going from hexane to acetonitrile.[17] If one assumes that dipole considerations are dominant and the mode of coupling is from the nitroxyl-oxygen to the sulfinyl-sulfur, then increased solvent polarity would have the opposite reactivity effect on the two reaction partners. The effect is evidently quantitatively larger for the nitroxyl than for the sulfinyl, but the calculations confirm the electronic nature of the moderated solvent effect.

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