

Mechanisms of Excited State Quenching by Aromatic Sulfoxides¹

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Aromatic sulfoxides quench singlet excited states of sensitizers whose singlet energies render energy transfer unlikely as a mechanism. Well over 50 rate constants for singlet quenching of various sensitizers by a series of sulfoxides have been obtained, as have estimates of the redox potentials for the series of sulfoxides. These data strongly suggest that the mechanism for quenching involves electron transfer and/or exciplex formation. Charge (electron) transfer is from the sensitizer to the sulfoxide.

Introduction

Because of its utility in asymmetric synthesis, the sulfoxide is a functional group of increasing interest in the organic chemistry community. Its thermal chemistry is an active area of research and has been recently reviewed.^{2,3} In contrast, the photochemistry of the sulfoxide is underdeveloped.⁴ Though evidence of a number of intriguing phototransformations is ample, mechanistic information is meager, and we have undertaken a systematic study.

One poorly understood area of fundamental importance is the mechanism by which sulfoxides quench sensitizers that have been used to carry out various chemical reactions.^{5–7} The triplet energies of simple aromatic sulfoxides are fairly high, in the range of 75–81 kcal/mol, with the higher values reserved for alkyl aryl sulfoxides.⁸ These exceed the triplet energies of molecules which have been reported as sensitizers, such as benzophenone ($E_T = 69$ kcal/mol) and naphthalene ($E_T = 61$ kcal/mol), though chemical transformations occur nonetheless. For example, Shelton and Davis found that *tert*-butyl phenyl sulfoxide decomposed under sensitization with acetophenone ($E_T = 74$ kcal/mol), triphenylene ($E_T = 66$ kcal/mol), and anthraquinone ($E_T = 63$ kcal/mol).⁹

Anomalous sensitization can also occur from singlet states. Mislow and Hammond found that aryl methyl sulfoxide photoracemization could be brought about by naphthalene (Np) singlets.^{10–13} This remains the best documented case of sulfoxide sensitization. Rate constants of 3×10^7 to 2×10^8 M⁻¹ s⁻¹ were determined for the quenching of Np by several aryl methyl sulfoxides. Elegant experiments correlated the rate constants with sensitized racemization of the sulfoxide. Recognizing the apparently endothermic energy transfer, Cooke and Hammond suggested that Np-sensitized racemization of tolyl methyl sulfoxide might result from exciplex formation.^{12,13} Yet, there was no direct evidence for the exciplex and “use of electron-donating and -withdrawing substituents on the benzene ring failed to show a clear trend or a large variation in the quenching rate constants which would support the hypothesis that charge-transfer interactions are dominant.”¹³ Given the usually dramatic effect of small energetic changes on rate constants in the reported range, such insensitivity is surprising. To more rigorously examine the mechanism(s) of sulfoxide quenching, a greater spread of related compounds was needed, and the rate constants so obtained needed to be correlated with other physical parameters.

We have conducted an extensive set of measurements with a matrix of sensitizers and substituted alkyl aryl and diaryl

sulfoxides that significantly substantiates electron transfer and/or exciplex formation as the mechanism by which the sulfoxides quench the singlet states of the sensitizers. Quenching rate constants were determined by single photon counting. Electrochemical properties of the sulfoxides were determined by cyclic voltammetry. Though the oxidations and reductions were found to be irreversible, the data clearly show that a charge transfer from the sensitizer to the sulfoxide is involved in excited state deactivation.

Experimental Section

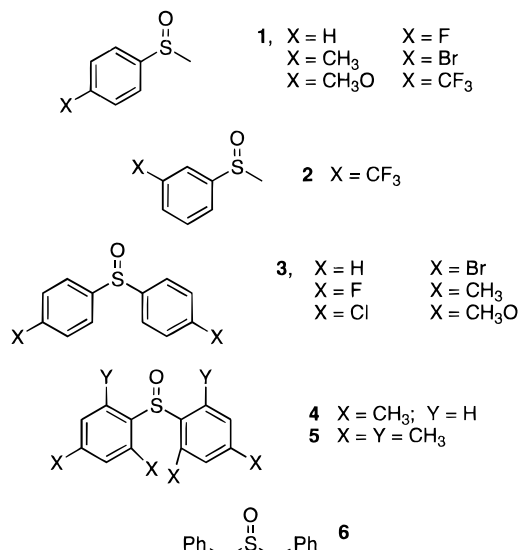
General. Commercially available sensitizers and sulfoxides were repetitively recrystallized from ethanol until GC traces indicated a purity of $\geq 99.9\%$. Acetonitrile for electrochemical measurements was held at reflux over calcium hydride until required and then distilled under dry argon for each use. Solvents for spectroscopic measurements were the highest grade available and used as received. UV/vis spectra were obtained on a Shimadzu 2101-PC spectrometer. NMR spectra were obtained on a Varian VXR 300 MHz instrument. The preparation of 1-CF₃ and 2-CF₃ from their corresponding sulfoxides is described in the Supporting Information. All other sulfoxides were commercially available or have been described previously.⁸

Single Photon Counting Measurements. All spectra and luminescence lifetimes were recorded with an Edinburgh Instruments FL-900 single photon counting fluorometer. The sample temperature was regulated at 21 ± 1 °C for all experiments. Solutions for luminescence lifetime measurements were prepared in acetonitrile or benzene to have a sensitizer absorbance of 0.1–0.3 at the excitation wavelength and were purged with argon for 10 min to remove oxygen. Quenching rate constants were determined by measurement of the fluorescence lifetime of the sensitizer as a function of sulfoxide concentration.

Electrochemical Measurements. The electrochemical setup consisted of a working electrode (gold or glassy carbon, 20 mm²) supported in a Pine Instruments rotator and connected to a Pine Instruments RDE4 potentiostat. The applied potential, measured against the saturated calomel electrode (SCE) with a platinum coil auxiliary electrode, was scanned at 200 mV/s over the required range under computer control. Measurements were performed in dry acetonitrile containing sodium perchlorate as the supporting electrolyte for the oxidations and tetrabutylammonium bromide for the reductions. Electrolyte concentrations were 200 mM, and substrates were 5–10 mM. Samples were purged with nitrogen gas to remove oxygen.

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CHART 1



Results and Discussion

The sulfoxides used in the present study are illustrated in Chart 1. The rate constants for quenching of singlet Np and various other sensitizers are shown in Table 1. Excellent agreement was obtained in the cases that overlap with Cooke and Hammond (quenching of Np by 1-H, 1-CH₃, and 1-Br in CH₃CN). The rate constants for Np were measured in both benzene and acetonitrile to check for effects due to the polarity of the solvent, but no systematic difference was found. Measurements with pyrene were limited by low rate constants and sulfoxide solubility.

Estimated oxidation and reduction potentials were determined by cyclic voltammetry.¹⁴⁻¹⁶ Under these experimental conditions, all of the oxidations and reductions were found to be irreversible. However, the peak potentials were found to be essentially insensitive to voltage scan rates, indicating rapid electron transfer. In Table 1 are listed the potentials corresponding to 50% of the peak oxidation or reduction current after accounting for background (half-peak potentials, $E_{pk/2}$), rather than true thermodynamic $E_{1/2}$ or E° values. It is presumed that the relative error for this series of compounds is small using this approximation. Peak potentials and representative CV traces are available as Supporting Information.

The rate constants for quenching of Np by the sulfoxides were plotted against their respective oxidative and reductive $E_{pk/2}$ values. Moderate correlation was observed against the reductive values, but no correlation whatsoever was observed against the oxidative values. In addition to redox quenching mechanisms, energy transfer was considered. The sulfoxides do not fluoresce, and many of them have long tailing absorption spectra. This combination makes determination of their singlet energies difficult. However, even allowing for a low energy 0,0 transition, Förster energy transfer can be eliminated on the basis of insufficient spectral overlap. In contrast, exchange (Dexter) type energy transfer does not require significant oscillator strength in the absorption and must be considered. Given the difficulty in establishing the singlet energies, the wavelength at which the molar absorptivity (extinction coefficient) of the sulfoxide reached 1000 M⁻¹ cm⁻¹ was used as an arbitrary surrogate. The correlation of the rate constants with this value is shown in Figure 1. (The singlet energy of Np corresponds to about 314 nm, which is about 4 kcal/mol lower energy than 300 nm.) It was found empirically that the correlation was better as the arbitrarily chosen extinction coefficient was lowered and

that there was no correlation between rate constants and λ_{max} of any absorption band. Though there is a significant correlation in Figure 1, the falloff in rate constants is far too gradual on the high-energy side, and no type of energy transfer is likely to accommodate the current data.

It would be difficult to draw firm conclusions about a general mechanism with only the rate constants for Np quenching. This is essentially the same problem run into by Cooke and Hammond, even though we have three times the number of sulfoxides. Additional rate constants measured with the other sensitizers, however, shed light on the problem. The relevant photophysical parameters for the sensitizers are presented in Table 2.

The energetics of photoinduced electron transfer in the "normal" region can be approximated for a related series of compounds by¹⁷

$$\Delta G_{et} = -E^* + E_{ox}(D) - E_{red}(A) - C$$

where E^* is the excitation energy of the sensitizer, E_{ox} and E_{red} are thermodynamic redox potentials, and C is a term which takes into account electrostatic energy, though other structural factors appear to add a constant offset.¹⁸⁻²⁰ In acetonitrile, C is typically ignored because of the high dielectric constant. If electron transfer is endothermic, then ΔG_{et} represents a minimum activation energy, though an additional reorganization energy is typical. A plot of the observed rate constants versus ΔG , calculated as above, is shown in Figure 2. No similar correlation is observed for oxidation of the sulfoxides and reduction of the sensitizers.

As plotted in Figure 2, the data are consistent with an electron transfer and/or exciplex formation mechanism for quenching of these sensitizers by sulfoxides. The solid curve in Figure 2 is a fit of all of the acetonitrile rate constant data to the Rehm-Weller equation,¹⁷ which yields a reorganization energy $\Delta G^\ddagger(0)$ of 4.2 kcal/mol. Despite the qualitative agreement with the Rehm-Weller model, there remains significant scatter in the data. Some of this may be due to the uncertainty in the reduction potentials of the sulfoxides as only $E_{p/2}$ values are available.

Like the previous work,¹³ none of the data presented here directly supports exciplex formation. In no case, in either acetonitrile or benzene, was exciplex luminescence detected. However, it must also be emphasized that lack of observation of luminescence does *not* rule out exciplex formation. Transient absorption spectra were not examined for exciplexes. The lack of exciplex fluorescence and high quantum yields of racemization measured by Cooke and Hammond^{12,13} make it seem unlikely that any long-lived intermediates would be detected.

In the above discussion it has been assumed that the quenching mechanisms for the various sulfoxides and sensitizers is essentially the same. For example, we assume that it is not true that electron transfer is the quenching mechanism in some cases and energy transfer in others. Although such pathological results are not out of the question, we would demand stronger evidence to draw such a conclusion.

Summary and Conclusion

Aromatic sulfoxides are found to quench aromatic sensitizers whose singlet energies are significantly lower than their own. Observed rate constants vary from diffusion controlled to 3 orders of magnitude lower. The rate constants for quenching of Np by diaryl sulfoxides are about an order of magnitude higher than those for the corresponding aryl methyl sulfoxide, but further conclusions based only on Np quenching are difficult

TABLE 1: Singlet Quenching Rate Constants and Redox Potentials for Various Sulfoxides

sulfoxide	k_q ($10^7 \text{ M}^{-1} \text{ s}^{-1}$) ^a					$E_{\text{pk}/2}$ (V) ^b	
	naphthalene	naphthalene	1-aminonaphthalene	pyrene	2,3-dimethylnaphthalene	reducn	oxidn
	C ₆ H ₆	CH ₃ CN	CH ₃ CN	CH ₃ CN	CH ₃ CN		
1-H	3.4 ± 0.1	4.5 ± 0.1			1.8 ± .1	−2.47	1.9
1-CH ₃	3.47 ± 0.04	4.5 ± 0.1			1.5 ± .1	−2.35	1.82
1-CH ₃ O	0.98 ± 0.01	< 1			0.42 ± 0.03	−2.68	1.73
1-F	2.4 ± 0.1	2.9 ± 0.1			0.70 ± 0.06	−2.52	1.89
1-Br	63.5 ± 2.4	74.2 ± 4.4			68.2 ± .2	−2.13	1.97
1-CF ₃	246 ± 8	202 ± 2	1160 ± 30		545 ± 20	−2.11	2.00
2-CF ₃	63 ± 1	67.1 ± 1.6	1110 ± 20		150 ± 10	−2.22	2.00
3-H	56.7 ± 1.6	76.9 ± 7.2	704 ± 8		37 ± 7	−2.26	2.00
3-F	32.0 ± 0.4	51.8 ± 2.3	785 ± 25		22.1 ± 0.02	−2.14	2.01
3-Cl	267 ± 5	264 ± 3	1150 ± 16		560 ± 20	−2.02	2.07
3-Br	590 ± 29	368 ± 17	1270 ± 20		810 ± 50	−1.88	2.05
3-CH ₃	46.7 ± 1.8	47.2 ± 1.1	483 ± 14		19 ± 1	−2.39	1.88
3-CH ₃ O	32.1 ± 0.1	33.4 ± 0.7			12.8 ± 0.2	−2.48	—
4	134 ± 5	152 ± 3	475 ± 14	≤ 1	68 ± 2	−2.37	1.82
5	720 ± 25	446 ± 25	325 ± 6	ca. 2	580 ± 40	−2.35	1.58
6	1.06 ± 0.03	< 1				−2.68	2.19

^a Quoted errors are standard deviations of the fit. ^b Values are relative to SCE. See text for further details.

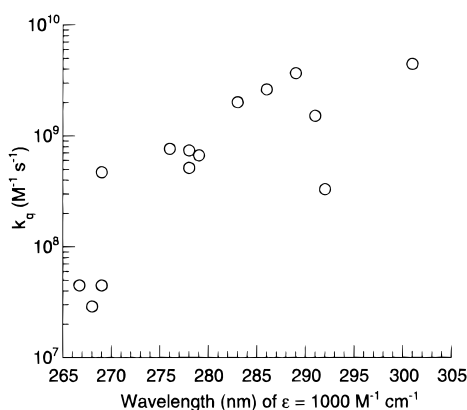


Figure 1. Rate constants for the quenching of singlet naphthalene plotted against the wavelength at which the sulfoxide molar absorption coefficient reaches $1000 \text{ M}^{-1} \text{ cm}^{-1}$.

TABLE 2: Photophysical Parameters of the Sensitizers²¹

sensitizer	spectroscopic singlet energy ^a (eV)	potential (V)	
		oxidn ^b	redn ^c
naphthalene	3.99	1.54	−2.49
1-aminonaphthalene	3.37	0.54	
2,3-dimethylnaphthalene	3.87	1.35	−2.64
pyrene	3.33	1.16	−2.09

^a In polar solvent. ^b In acetonitrile, *vs* SCE. ^c In DMF, *vs* SCE.

to draw. However, the overall rate constant profile for a series of sulfoxides and sensitizers is consistent with an electron transfer and/or exciplex mechanism for quenching. Estimates of the oxidation and reduction potentials of the sulfoxides, based on irreversible cyclic voltammetry waves make it clear that the direction of charge transfer is from sensitizer to the sulfoxide.

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Supporting Information Available: Table listing the oxidation and reduction peak potentials for all sulfoxides, text detailing the preparation and characterization of 1-CF₃ and

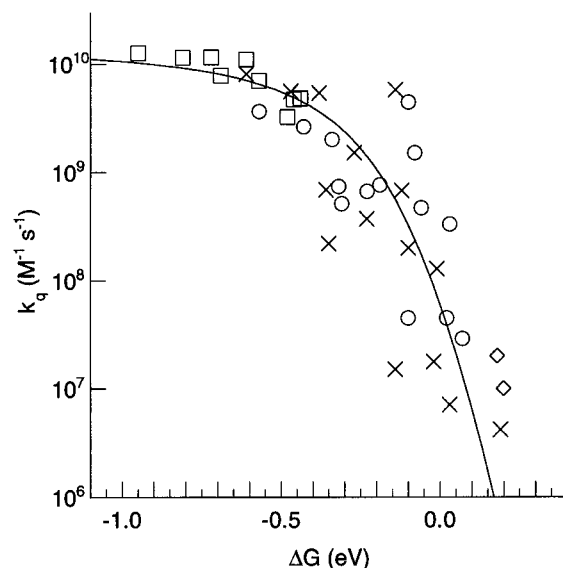


Figure 2. Rate constants for quenching of various sensitizers by the sulfoxides plotted against ΔG for electron transfer (see text.) The squares correspond to 1-aminonaphthalene, the circles are naphthalene, the crosses are 2,3-dimethylnaphthalene, and the diamonds are pyrene.

2-CF₃, and a figure showing representative CV traces (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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