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Photophysics and stereomutation of aromatic sulfoxides

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Photophysics and stereomutation of aromatic sulfoxides

by

Woojae Lee

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Organic Chemistry

Major Professor: William S. Jenks

Iowa State University

Ames, Iowa

2000

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ABSTRACT

Aromatic sulfoxides are photochemically active molecules. At 77 K in ether/isopentane/ethanol (EPA) glass, aromatic sulfoxides are shown to have weak phosphorescence. The triplet energies are a few kilocalories per mole higher than the corresponding ketones. The diaryl sulfoxides are about 3 kcal/mol lower than the corresponding ketones, and the diaryl sulfoxides are about 3 kcal/mol lower than the corresponding aryl methyl sulfoxides. The lifetimes of emission are generally under 100 ms. From the diffuse vibrational structure of the spectra, the lifetimes, and the effect of solvent on the triplet energy, it is concluded that the triplets are delocalized aromatic states that involve substantial charge transfer off the oxygen atom.

The effect of a methanesulfinyl group on the photophysics of several aromatic chromophores has been investigated. Compared to the parent arenes, the spectroscopic singlet energies and the triplet energies are relatively unchanged by the substitution (±2 kcal/mol). The fluorescence quantum yields are reduced by at least one order of magnitude, whereas the phosphorescence quantum yields at 77 K are enhanced. Fluorescence lifetimes are greatly shortened, consistent with the reduced Φ_F. The triplet yields at room temperature are slightly enhanced by the substitution. Unusual fluorescence quantum yield enhancements are observed on cooling the samples to 77 K. For instance, a 15-fold increase of fluorescence of 1-methanesulfinylpyrene is observed upon freezing the sample whereas only a factor of 2 is seen in the unsubstituted pyrene. An attempt to relate the observed photophysics to photoinduced racemization is made, since the photoracemization is negligible at 173 K. Racemization yields as a function of temperature have also been obtained. For methanesulfinyl pyrene, the activation barrier of photoracemization is estimated to be 2-7 kcal/mol.

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 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.

CHAPTER I

PHOTOCHEMISTRY OF SULFOXIDES: A GENERAL REVIEW

1.1 Dissertation organization

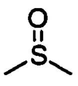
This dissertation contains five chapters. Chapter 1 is a literature review of the photochemistry of sulfoxides and a general description of the sulfoxide functional group. The main emphasis is on the stereomutation reaction, but the other major photochemical processes of sulfoxides are discussed. Chapter 2 and Chapter 4 are based on two independent published papers. Chapter 3 will be the basis for another publication.

Chapter 2 discusses the excited triplet state photophysics of various diaryl and alkyl aryl sulfoxides at cryogenic temperature. In Chapter 3, the effect on the photophysics of several aromatic chromophores by substitution of the methanesulfinyl group is discussed, with particular reference to stereomutation. In Chapter 4, an electron transfer and/or exciplex mechanism for quenching by aromatic sulfoxides is discussed in detail. Chapter 5 contains the general conclusions and a summary of the previous four chapters.

While the great majority of the work described here was carried out by the author, there were contributions from other group members. Some of the sulfur compounds studied in Chapter 2 were prepared by David Shutters and Dr. William Jenks. Also, the EPR measurement was done by Professor Jenks. The quantum yields of triplet formation by measured laser flash photolysis at room temperature in Chapter 3 were obtained by Dr. Alex Darmanyan. Oxidation and reduction potential measurements in Chapter 4 were carried out by Dr. Paul Charlesworth.

1.2 Fundamental properties of sulfinyl group

The sulfoxide functional group (or sulfinyl group) in some ways can be considered a carbonyl analog. For instance, the polarization of the S-O and C-O bonds is similar, both stabilize α-carbanions, and α-cleavage is one of the main photochemical processes of both functionalities. Even though the sulfinyl group has common features with the carbonyl, it has just as many fundamental differences. The different pattern of hybridization of the sulfur is the fundamental cause of this. While the carbon atom has sp^2 hybridization in the carbonyl group, the sulfur has approximately sp^3 hybridization in the sulfinyl group. Unlike the carbonyl group, no distinct π bond is found between sulfur and oxygen atoms. The sulfur-oxygen bond, however, is not a simple sigma bond, either. Because of the complexity of sulfur-oxygen bond, a meaningful simple orbital description has not been universally settled upon. Partly for this reason, there are several ways used to represent the sulfoxide. An ylide form (structure **3**) where the electron density is localized on the oxygen atom represents many aspects of the sulfoxide reasonably accurately. With aid of computation, however, it is clear that the sulfur atom in a sulfoxide does not have three equivalent sp^3 hybridized bonds and a lone pair. The CSC bond angle of dimethyl sulfoxide (DMSO) is calculated to be about 95°, which is considerably narrower than the ideal sp^3 hybridization angle.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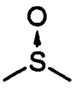
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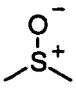
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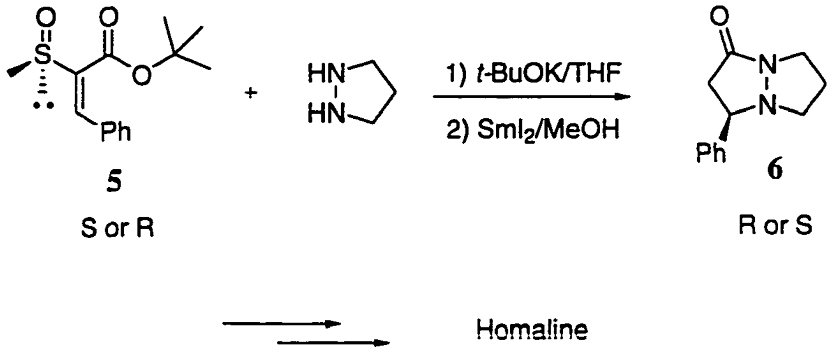
Structure **1** is the most commonly used drawing for sulfoxides in most of the literature. For consistency, it is chosen for use in this dissertation. Structure **4** contains an expression of stereochemistry. Structure **4** (or ylide-based equivalent) is a useful representation when stereochemistry is being emphasized, but it should be made clear that all of these drawings are representations of the same thing.

An important feature of sulfoxides is their stereochemical stability. The inversion barrier for most compounds is >35 kcal/mol.[1] Due to this feature, chiral sulfoxides have been used extensively as versatile chiral auxiliaries in organic synthesis.[2-7] Usually a resolved chiral sulfoxide is used to induce another stereogenic center into an adjacent part of the molecule, so that a particular diastereomer is formed. Then, at a later stage, it is removed



Scheme 1. The synthesis of homaline from a chiral sulfoxide.

from the molecule. Scheme 1 shows an example in which a chiral sulfoxide was used as a chiral auxiliary for a synthesis of homaline.[8]

Sulfur can have various oxidation states, of which the sulfoxide is an intermediate case. The sulfoxide can be readily either oxidized to the sulfone or reduced to the sulfide. Each of these functional groups has distinct thermodynamic and photolytic properties. Several different but related sulfur functional groups and their nomenclatures are listed in Figure 1.

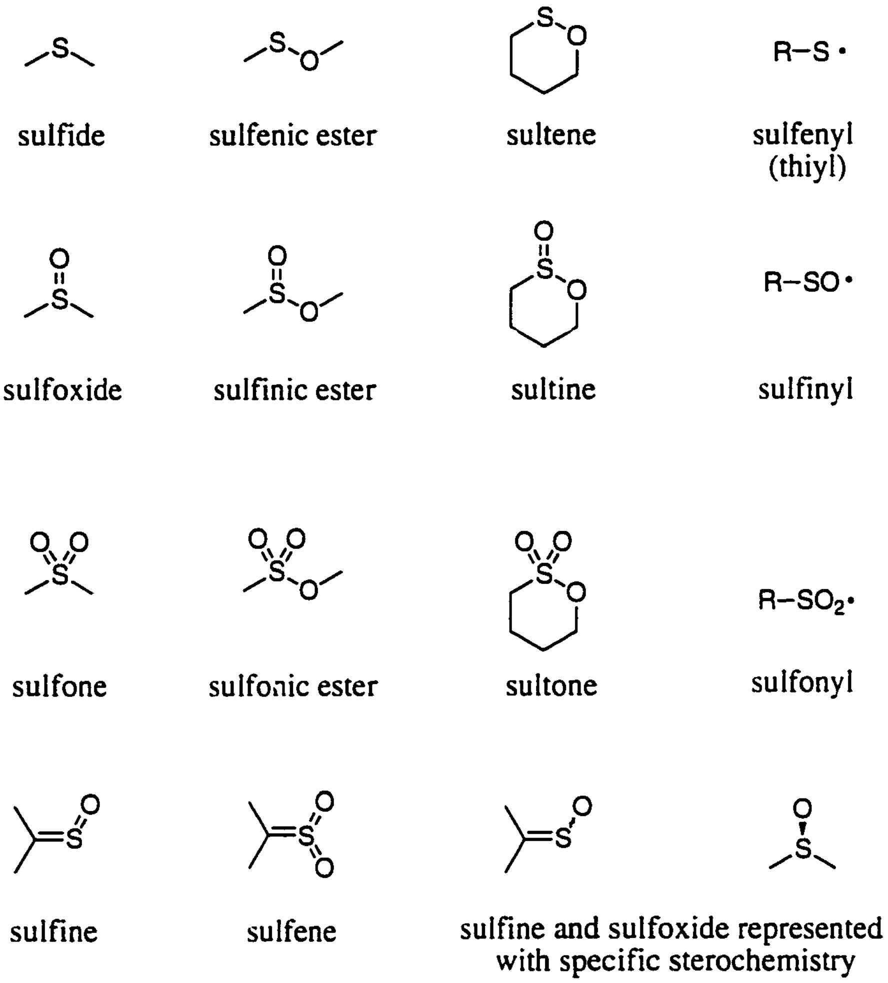


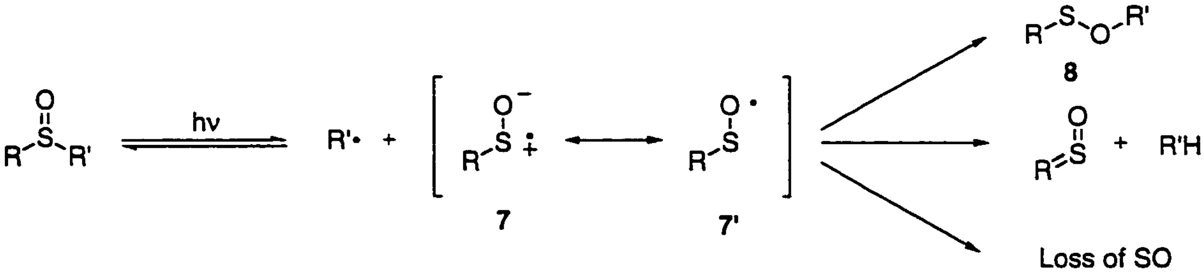
Figure 1. Illustration of sulfur-containing functional groups.

1.3 Review of photochemistry of sulfoxides

The main purpose of this research is to characterize the photophysics of sulfoxides and to determine the relationship between their photophysics and stereomutations reactions. Therefore, sulfoxide systems that mainly do photophysics and racemization (i.e. little other photochemistry) were designed and investigated in this dissertation. Since stereomutation is one of the main interests, both photochemical and thermal racemization will be discussed in this chapter along with chemical racemization. Even though no other significant photochemical processes were observed in the sulfoxide systems studied in this dissertation, it is worthwhile to review briefly the other important photochemistry of sulfoxides. α-Cleavage, hydrogen abstraction, and deoxygenation reactions of sulfoxides will be reviewed from the literature.

1.3.1 α-Cleavage

α-Cleavage, the homolytic carbon-sulfur bond cleavage, is the most common photochemical process in the sulfoxide system. When a sulfoxide is photolyzed, α-cleavage results in the formation of sulfinyl radical **7**, which has two important resonance structures, and a carbon radical in the solvent cage. If the sulfoxide is cyclic, a biradical is formed instead of a radical pair.

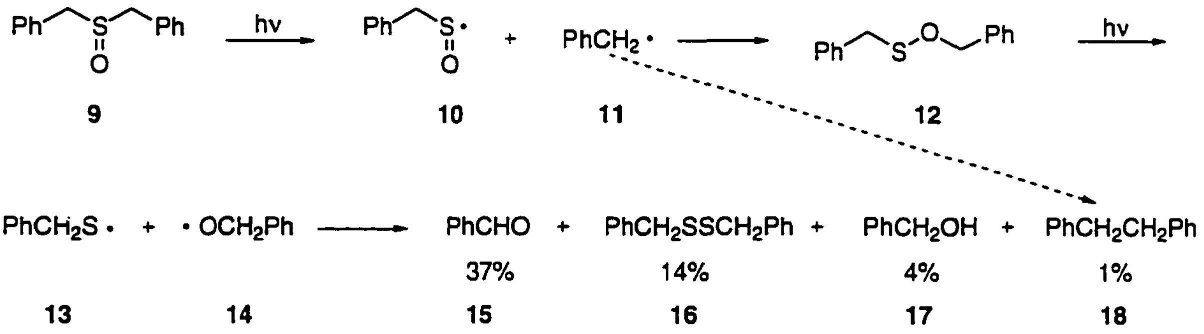


At this stage in the process, several different reactions can occur. The two radicals can recouple to go back to the starting sulfoxide. If the starting material is chiral, the recoupling of radicals results in racemization. Coupling between the organic radical and oxygen terminus of the sulfinyl radical (7') within the solvent cage produces the sulfenic ester, **8**. When the radicals escape from the solvent cage, additional reactions can occur such as coupling of carbon radicals or sulfinyl radicals.

Evidence for α-cleavage has been reported using several different methods. Several arenesulfinyl radicals and their spin trapping products were detected directly by steady state electron paramagnetic resonance (EPR) experiments at low temperature.[9-13] Chemically induced dynamic nuclear polarization (CIDNP) was also used to investigate α-cleavage pathways of sulfoxide photolyses.[14,15] By laser flash photolysis, the phenyl sulfinyl radical transient was directly obtained at room temperature and the radical was studied computationally.[16] Below, α-cleavage with four subcategories is reviewed in more detail: benzylic and allylic systems, dialkyl systems, aryl alkyl and diaryl sulfoxides, and SO extrusion.

1.3.1.1 α-Cleavage of benzylic sulfoxides

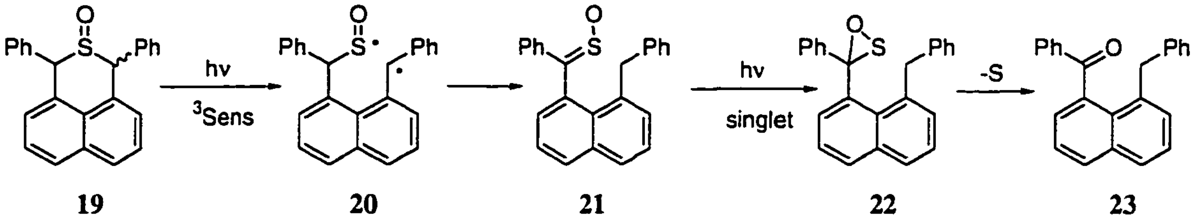
Dibenzyl sulfoxide is a dialkyl sulfoxide, but its photochemistry is closely related to the aryl alkyl and diaryl systems. The phenyl chromophore is not conjugated to the sulfoxide functional group and the observed photochemistry probably derives from the benzyl system more than sulfinyl group. Nonetheless, it was an early-investigated system and helps establish reactivity patterns. The α-cleavage reaction produces relatively stable radicals, benzyl sulfinyl radical **10** and benzyl radical **11**.

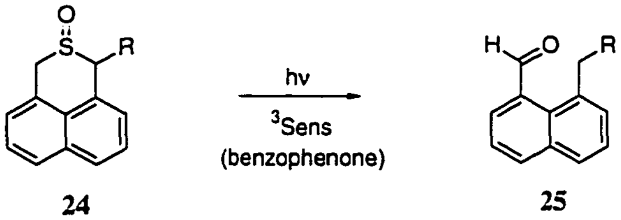


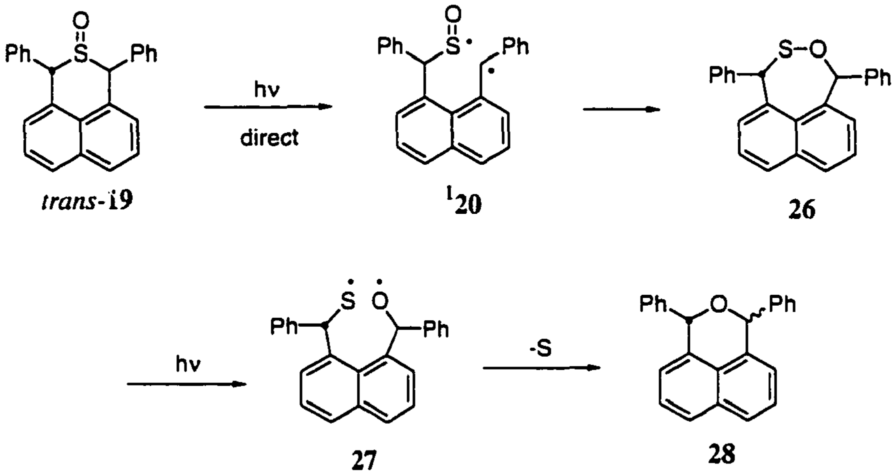
The photolysis result of dibenzyl sulfoxide was reported by Sato and co-workers in the mid 1960s.[17,18] The main products were benzaldehyde **15** in 37% yield and benzyl mercaptan, which was isolated as dibenzyl disulfide **16** (14%). The minor products were identified as benzyl alcohol **17** (4%) and bibenzyl **18** (1%), with trace of amount of *trans*-stilbene and phenanthrene. Even though no mechanism was proposed at the time, the product formation can be clearly explained by α-cleavage of the sulfoxide followed by secondary photolysis of sulfenic ester **12**.

Based on the work described in Chapter 2, the triplet energies of sulfoxides (near 80 kcal/mol for aryl alkyl sulfoxides and 75-78 kcal/mol for diaryl sulfoxides) are a few kcal/mol higher than those of ketones.[19] Before this was known, there were several literature reports in which a ketone was used to photosensitize the sulfoxide. Work performed by Schultz and Schlessinger overcame this flaw by using the naphthyl system to lower triplet energies of sulfoxides. For instance, the triplet energy of 1-methanesulfinyl naphthalene is 60 kcal/mol (measured and described in Chapter 3).

The photolysis of a mixture of stereoisomers of sulfoxide **19** with a triplet sensitizer produced a mixture of stereoisomers of sulfines **21**, presumably through the diradical that is formed by α-cleavage of the sulfoxide.[20] The final product, the desulfurized ketone **23**, was produced through the singlet sulfine chemistry.[20,21] (The triplet photochemistry of the sulfine is only interconversions of stereoisomers.) Under the same photolysis conditions, ketone product **25** was isolated from asymmetric sulfoxides **24**.[22] The first step of the photoreaction was also α-cleavage of the sulfoxide. Cleavage occurred on the side to form the more stable biradicals.







Direct irradiation of sulfoxide **19** forms dramatically different products from those of sensitized photolysis.[23] Along with the photoisomerization, two new photoproducts were formed by the direct irradiation. The photolysis of *trans* **19** in the presence of triplet quenchers yielded the *trans* sultene **26** with high efficiency. Secondary photolysis of **26** resulted in the formation of mixtures of ether stereoisomers **28**. This clearly shows the difference in reactivity depending on the spin state of the sulfinyl biradical.

Recently, Guo and Jenks examined the photolysis of phenyl benzyl sulfoxides to clarify the mechanism of α-cleavage.[24] The photolysis of sulfoxide **29** at short wavelength (e.g., 254 nm) produced compound **31** by an α-cleavage reaction in which radical pair **30** and **11** were formed. Due to its secondary photolysis, compound **31** was not observed in the product mixture using irradiation at longer wavelengths. The radical pair also gave the starting material back with racemization and small amount of escape products **33** and **34**. Triplet sensitization by acetone dramatically increased the formation of escape products. Thus, it was concluded that the primary process on direct irradiation was α-cleavage from the

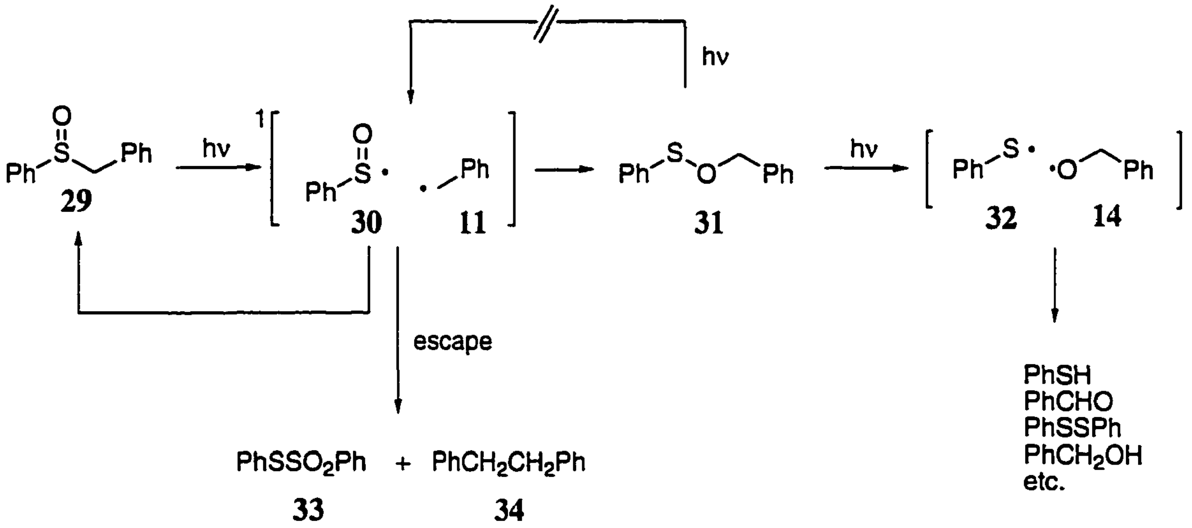


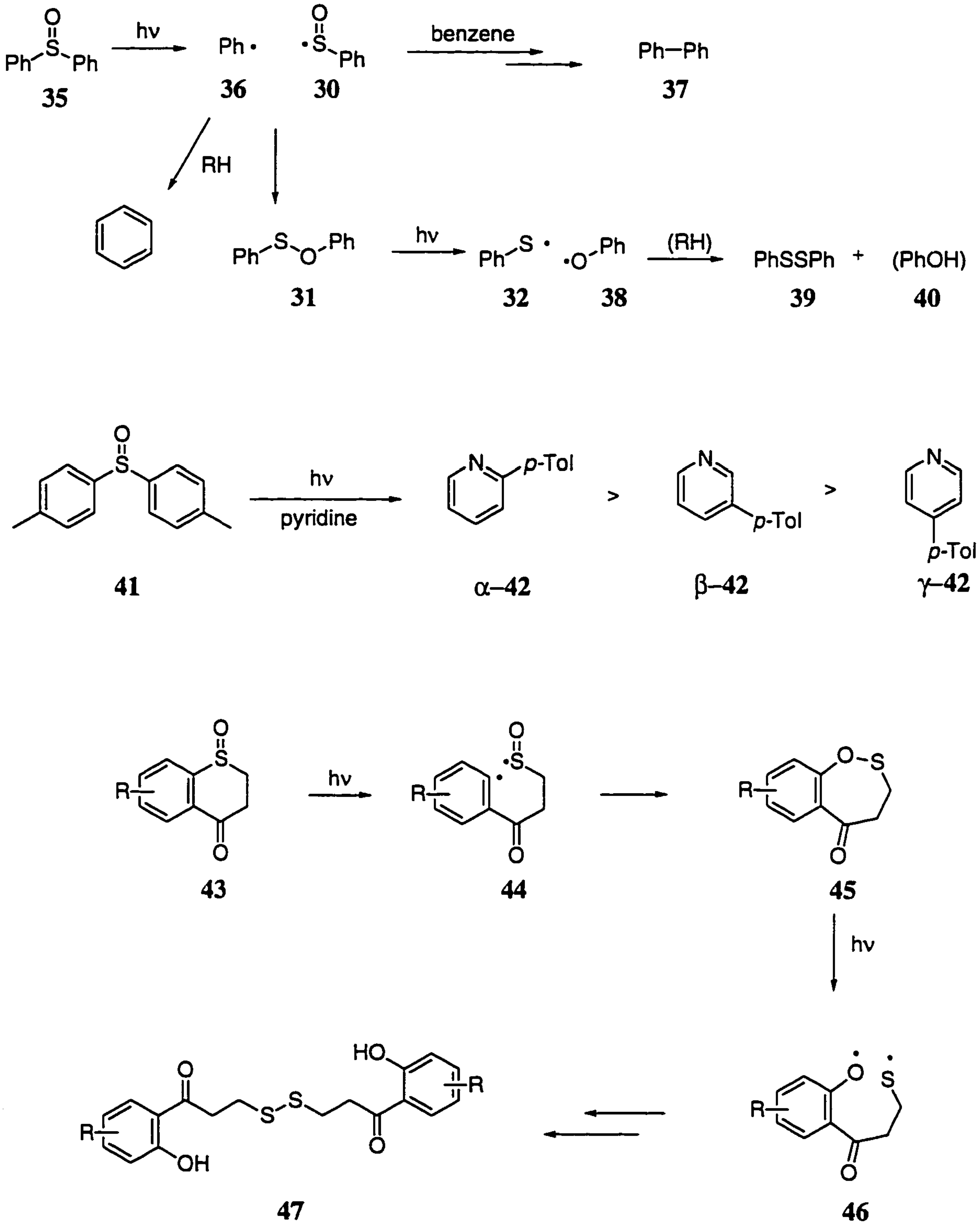
Figure 2. Mechanism for the photolysis of phenyl benzyl sulfoxide.

singlet state of **29**. Also, they showed that the photolysis of compound **31** led exclusively to S-O homolysis without the observation of O-C cleavage.

1.3.1.2 α-Cleavage of alkyl aryl and diaryl sulfoxides

There have been several investigations of sulfoxide photochemistry on various diaryl and aryl alkyl sulfoxide systems.[25,26] The clear difference of diaryl and dialkyl sulfoxides from dialkyl sulfoxides is their bathochromic shift in UV absorption due to conjugation to the aryl chromophore. Such work is briefly reviewed here.

The first photolysis of diaryl sulfoxide was reported by Kharasch and Khodair.[27] In benzene solution, the photolysis of diphenyl sulfoxide **35** gave biphenyl **37** (53%), diphenyl sulfide (7%), and a trace amount of diphenyl disulfide **39**. The formation of biphenyl was explained by the reaction between photochemically generated phenyl radical and benzene solvent. The formation of disulfide may be explained by the formation of phenyl benzenesulfenate followed by its secondary photolysis. The combination between photochemically generated phenyl radicals and solvent was clearly shown in the work done by Nakabayashi and co-workers.[28] The photolysis of di-*p*-tolyl sulfoxide **41** in pyridine solvent leaded to form *ortho-*, *meta-*, and *para-*(*p*-tolyl) pyridine.



R = Electron donating group

Figure 3. Photolysis of sulfoxide with electron donating group on aryl ring.

In the 1970s, Still and co-workers have studied on the photochemistry of derivatives of thiochromanone sulfoxide.[29-31] Even though there is a carbonyl group in the molecule, the photochemical behavior is strongly affected by the presence of sulfinyl group.[26] Depending on the substitution patterns, three major reaction types were established.[31]

The first reaction type was observed when electron releasing groups are substituted on the aryl ring (Figure 3). The photolysis of sulfoxide **43** yielded only 10% of product disulfide **47** apparently via a surprising aryl-S cleavage, while the rest of products were uncharacterizable. The labeling of ^{18}O of sulfoxidic oxygen of starting sulfoxide **43** resulted in the phenolic oxygen in the product **47**.

The second reaction type was observed when the β position to the sulfoxide was substituted (Figure 4).[29] Products **55** and **56** were produced from the secondary photolysis of compound **54**. Two different mechanistic pathways were proposed for this reaction. Both mechanisms were involved in the α-cleavage of sulfoxide. The difference between the two mechanisms was the orientation of the α-cleavage, either aryl-S or alkyl-S. In the first mechanism, alkyl-S scission gave the formation of sultene **50** and followed by S-O homolysis of sultene. The intermediate **54** was formed with a loss of sulfur atom, even though the mechanism for this step was not known. The other mechanism was the aryl-S

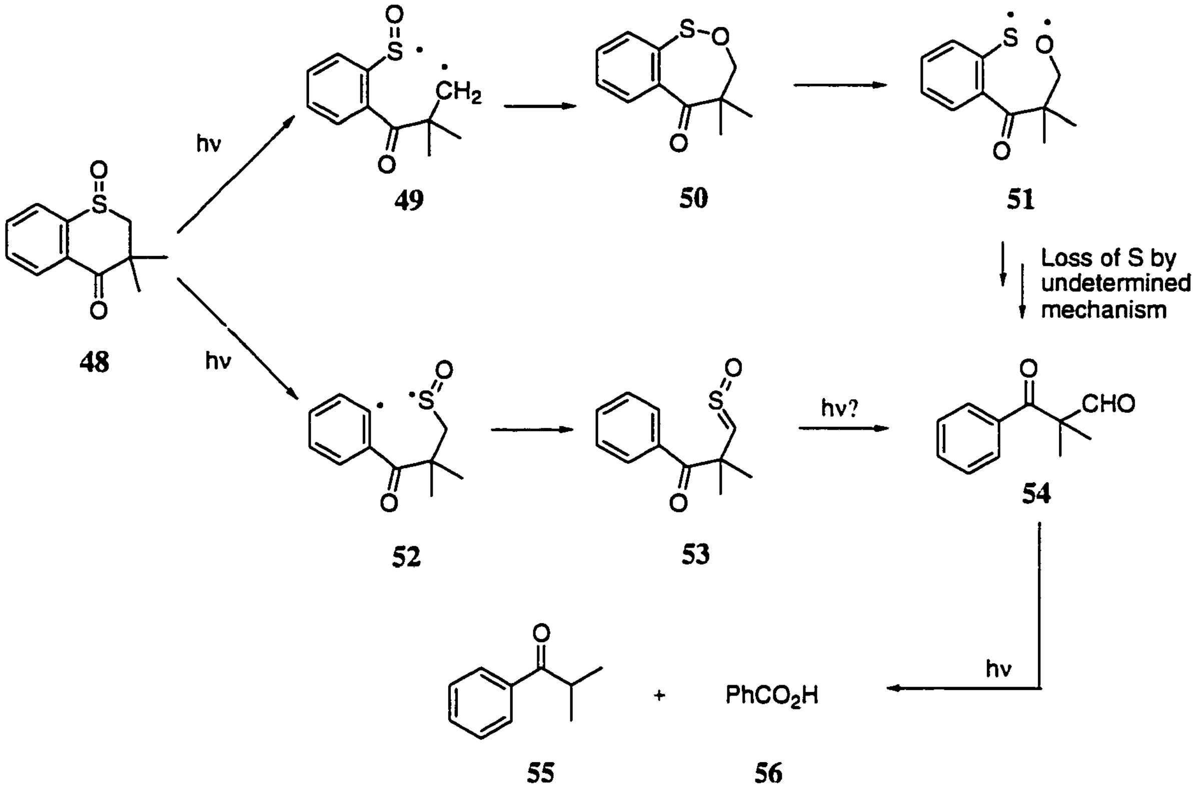
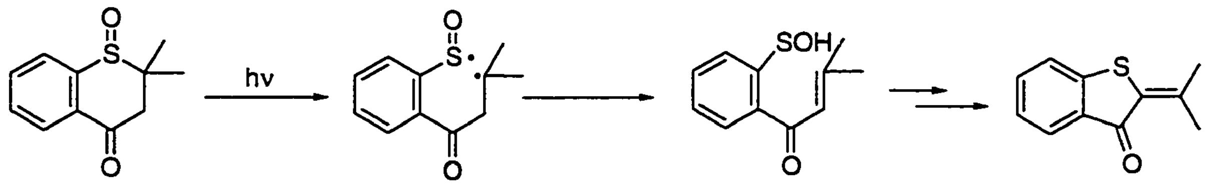


Figure 4. Photolysis of sulfoxide with the substitution on the β position of sulfoxide.

bond breaking, which resulted in the formation of sulfine **53**, followed presumably by photochemical desulfurization.[20,31]

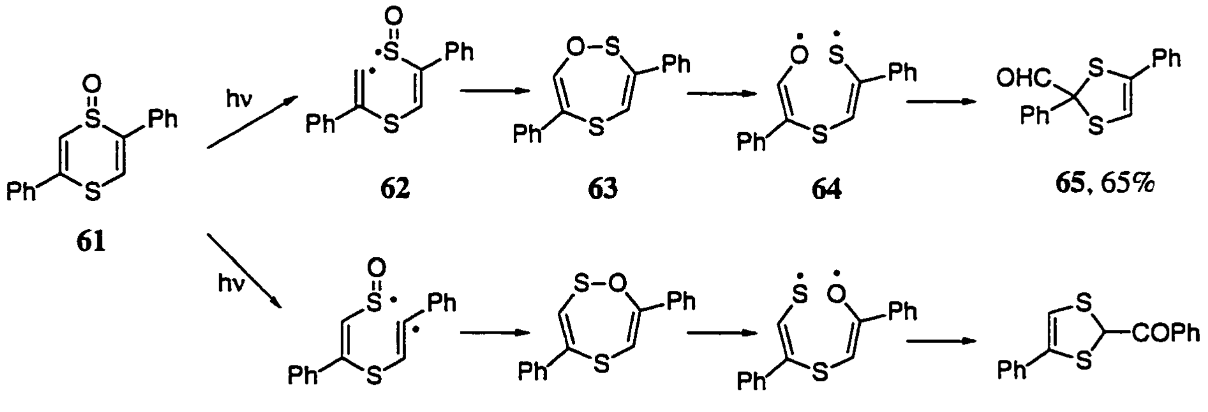
When the alkyl groups were substituted at the α-position to the sulfoxide, entirely different chemistry was observed (Figure 5). This third reaction type was explained by α-cleavage, but hydrogen abstraction mechanisms were also proposed.[29]



57 **58** **59** **60**

Figure 5. Photolysis of sulfoxide with the substitution on the α position of sulfoxide.

The photolysis of 1,4-dithiin sulfoxide system shows a very interesting result.[32,33] Unlike their thermochemisty, which showed the formation of thiophene via a net SO extrusion in polar solvent and ring contracting rearrangement to **65**, no extrusion was observed on photolysis. Instead, the other ring contracting rearrangement product **69** was observed in addition to **65**. Both products were rationalized by α-cleavage on either side of sulfur and the formation of sultenes **63** and **67**, followed by homolysis of S-O which resulted in the product formations.

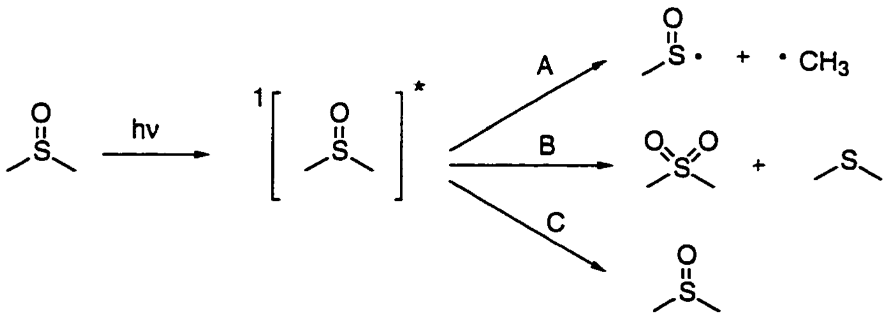


61 **62** **63** **64** **65**, 65% **66** **67** **68** **69**, 9%

Later, Jenks and Guo investigated the aryl alkyl sulfoxide system that produced primary, secondary, and tertiary alkyl radicals via α-cleavage reactions.[34] Benzyl, tertiary and secondary S-C homolysis is favored over Ph-S scission and primary C-S cleavage is comparable to Ph-S scission. They also observed the transient of sulfinyl radical by the laser flash photolysis.

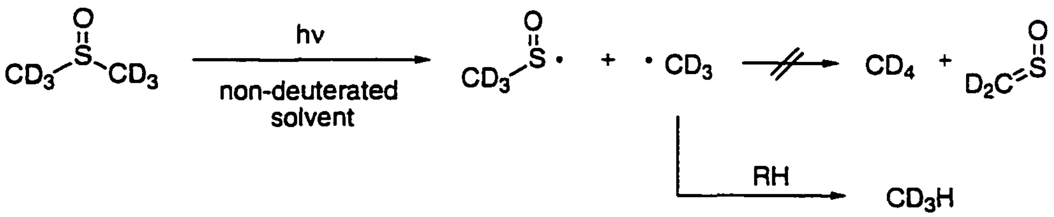
1.3.1.3 α-Cleavage of dialkyl sulfoxides

Following early work on benzylic sulfoxide system by Sato and Horner,[17,35] direct and sensitized photolysis of dimethyl sulfoxide (DMSO) was investigated in detail by Gollnick and Stracke.[36-38] There are three different processes postulated to occur from the singlet excited states of DMSO. This postulation came from the result that no effect was observed by using triplet sensitizers. This observation, however, was obtained when ketones were used as triplet sensitizers, which have lower triplet energies than DMSO.

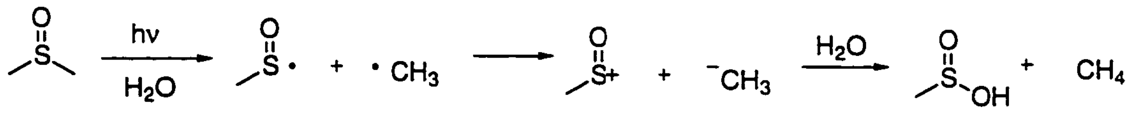


Path A represents the α-cleavage of sulfoxide which leads to form methanesulfinyl radical and methyl radical. Path B is a disproportionation reaction to sulfide and sulfone from two sulfoxides. Path C is the simply going back to the ground state of sulfoxide from the excited state in the high DMSO concentration.

The quantum yield of the α-cleavage was 0.14, independent of solvent. Isotope labeling experiments showed that there were important pathways in this reaction beside the α-cleavage mechanism. When DMSO was irradiated in *O*-deuterated alcohols, the molar ratio of formation of CH_4 to CH_3D varies from 1:1 in CH_3OD to 3:1 in CH_3CH_2OD to 11:1 in $(CH_3)_2CHOD$, which indicated existence of a non-radical mechanism for the formation of methane. Also, the photolysis of d_6-DMSO in non-deuterated solvents gave the formation of CD_3H exclusively, which was not the usual disproportionation reaction.



Based on the pH dependence of the quantum yield, the lack of ^{18}O exchange, the pattern of the H/D ratios, and the energetics of heterolytic cleavage, an electron transfer mechanism from methanesulfinyl radical to methyl radical which are formed from ordinary α-cleavage was proposed.

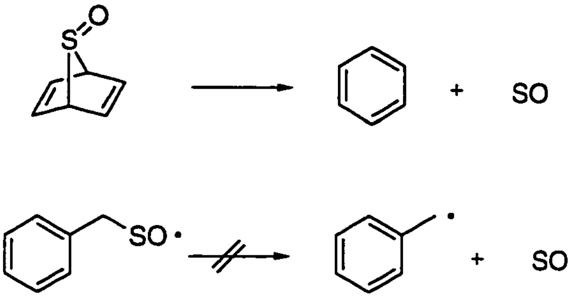


The formation of methyl radicals and SO from the gas phase photolysis of DMSO at 193 nm was reported using laser induced fluorescence (LIF) technique by Chen and co-workers.[39] The quantum yield of the formation of SO was near 1, but no methanesulfinyl radical was found. Later, the formation of methanesulfinyl and methyl radical was detected in the gas phase photolysis using molecular beam time-of-flight (TOF) mass spectrometry by Zhao and co-workers.[40] The photolysis of DMSO at 193.3 nm resulted in formation of methyl and methyl sulfinyl radicals as a stable primary products. Also, SO was detected, which originated mainly from the decomposition of methanesulfinyl radical. The quantum yield for the formation of methyl radical was 1.53. No scission between sulfur and oxygen was found.

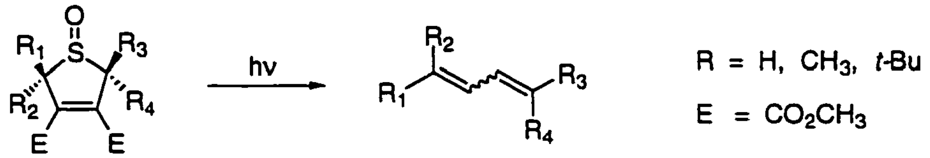
The solution phase photolyses of other dialkyl sulfoxides such as di-*t*-butyl sulfoxide, diisopropyl sulfoxide and so on were reported by Shelton and Davis.[41] In contrast to Gollnick and Stracke's work, the major product of the photolysis in some solvents was the corresponding sulfide without the detection of sulfone. Also, several other products that can be explained by α-cleavage were obtained. For example, the photolysis of di-*t*-butyl sulfoxide leaded to produce *t*-butanol, di-*t*-butyl disulfide, a small amount of acetone, and a trace amount of *t*-butyl *t*-butane thiosulfinate beside di-*t*-butyl sulfide.

1.3.1.4 SO extrusions

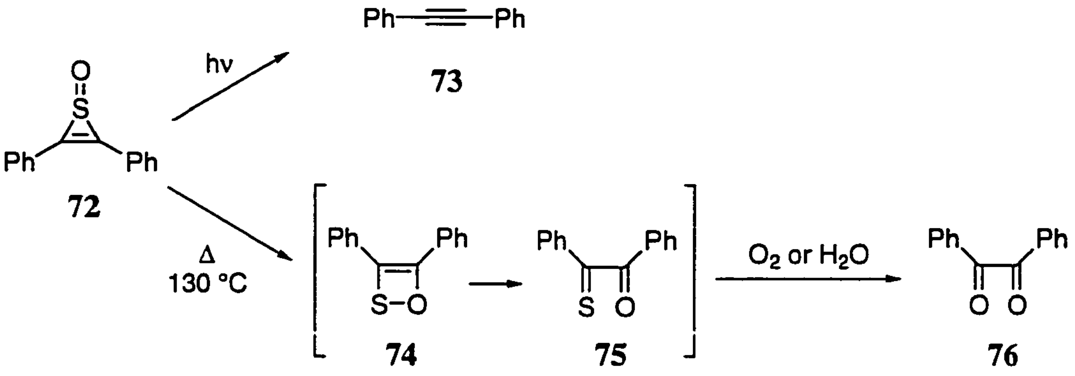
Photoextrusion of SO_2 in sulfones is a well-known reaction. Certain sulfoxides show the analogous phenomenon, SO extrusion, but it is not nearly as common as with sulfones. This presumably derives from the comparative stability of SO_2 and SO. The loss of SO from methanesulfinyl radical is estimated to be endothermic by 50 kcal/mol[42] so it is not observed at room temperature in solution.[11] The extrusion of SO is thought to be a stepwise reaction[25] and is only observed when there is a substantial driving force to cause the second C-S cleavage.



The first known SO extrusion was reported by Kellogg and Prins in 1974 in the dihydrothiophene derivatives system.[43] The thermal extrusion of the corresponding sulfone gave the stereospecific diene products, which implied a concerted mechanism. The photolysis of sulfoxides **70** produced the dienes **71** with mixtures of isomers, which strongly implied the formation of a biradical by stepwise α-cleavage reactions.



70 **71**



A few years later, Carpino and Chen showed the photolysis of 2,3-diphenylthiirene-1-oxide **72** gave diphenylacetylene **73** quantitatively.[44] Unlike the photolysis, the pyrolysis of **72** yielded only benzil. It is still unknown whether this is stepwise or concerted.

1.3.2 Hydrogen abstraction

Hydrogen abstraction has been well-established reaction in carbonyl photochemistry. Due to the analogy to carbonyl functional group, it also has been proposed as another primary process of sulfoxide photochemistry. Unlike the carbonyl, however, there is lack of evidence for hydrogen abstraction in sulfoxide photochemistry. Even though hydrogen abstraction provides a reasonable mechanistic pathway to rationalize some products, those also can be explained by α-cleavage.

Hydrogen abstraction usually has been proposed in cyclic sulfoxide systems. The formation of 2-isoproylbenzothiophene **113** from the photolysis of 2,2-dimethylthiochroman-

S-oxide **106** was observed by Archer and Kitchell.[45] β-Hydrogen abstraction was proposed to explain the product formation. (Figure 8) Two almost identical isoenergetic conformation were found by PM3 semi-empirical calculation and one of which is represented reasonably well by this drawing in the next page.

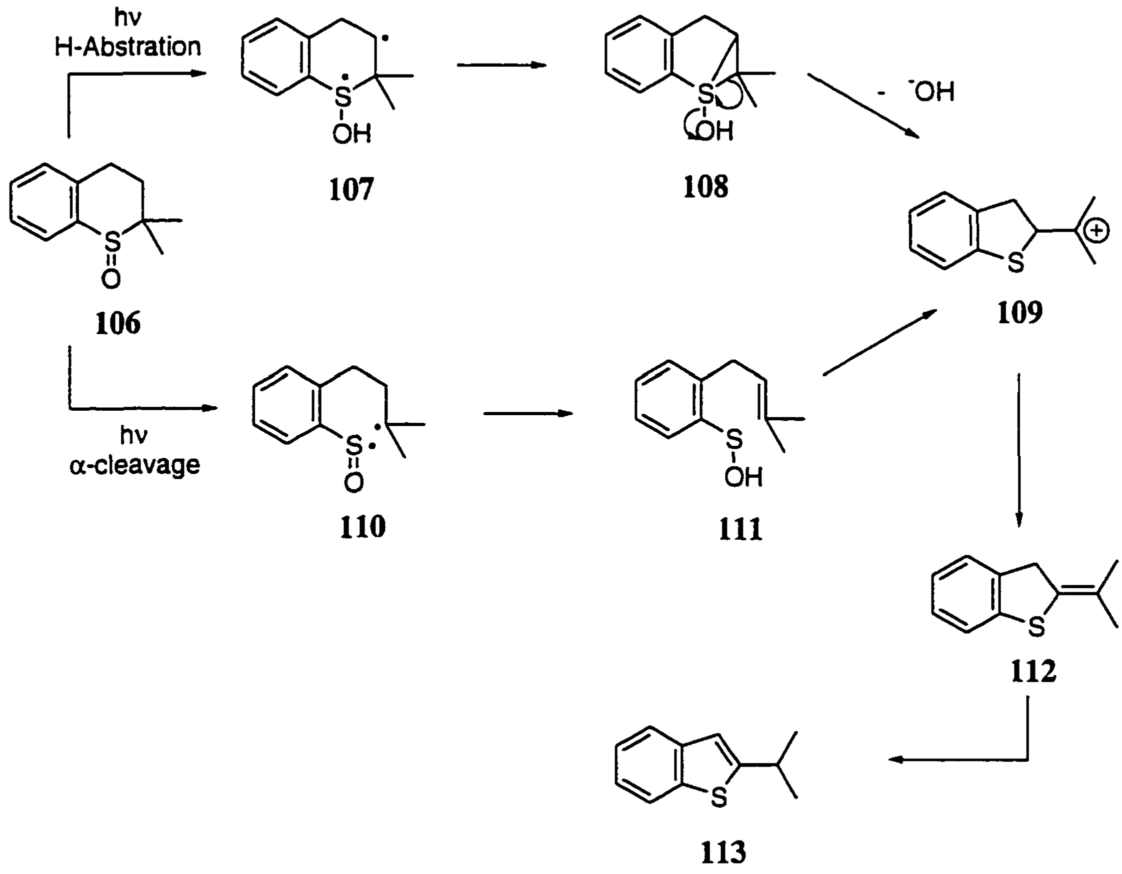
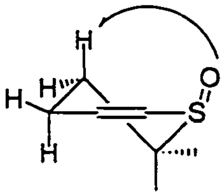
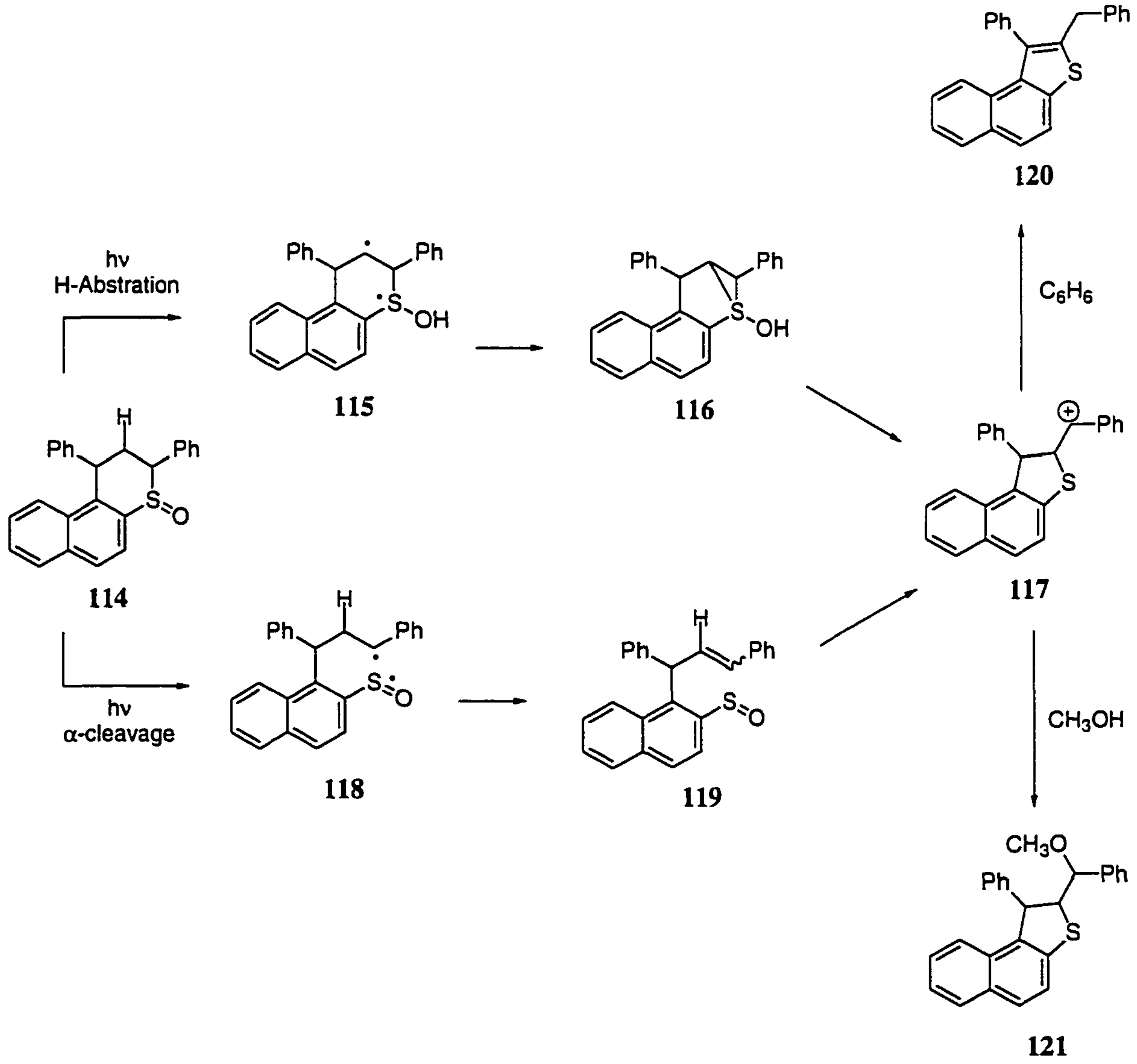


Figure 8. Hydrogen abstraction vs. α-cleavage in benzothiophene system.



105

benzo group deleted for clarity



The same β-hydrogen abstraction reaction was proposed in the conversion of sulfoxide **114** to thiophene **120** by Schultz and Schlessinger.[46] A deuterium labeling experiment showed that only the β-hydrogen was lost in the process in the scheme above. However, this process can also be explained by an α-cleavage mechanism.

In 1995, Guo and Jenks designed an experiment to obtain direct evidence for hydrogen abstraction.[24] The systems in Figure 9 were designed to favor β- and γ-hydrogen abstractions. There were no products isolated that could be formed only by a hydrogen abstraction mechanism.

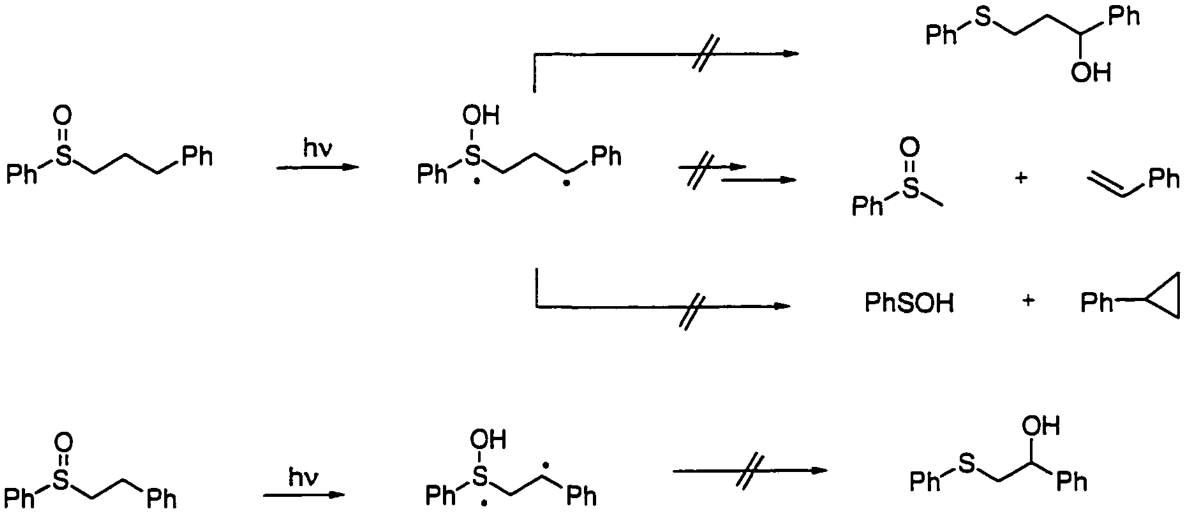


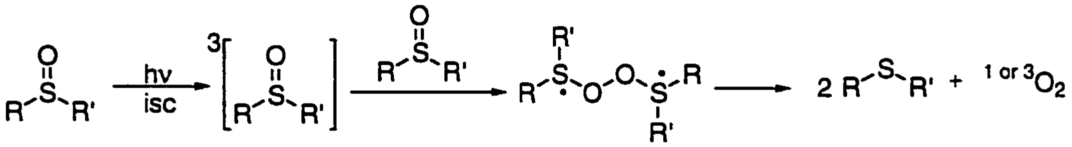
Figure 9. Possible hydrogen abstraction products

To date, there has not been any convincing evidence for hydrogen abstraction as a primary process of sulfoxide photochemistry. Though it cannot be completely ruled out, α-cleavage pathways should probably be considered as a first mechanistic alternative.

1.3.3 Deoxygenation

Deoxygenation is the reduction process from sulfoxides to sulfides. This phenomenon is not observed in ketone chemistry. There may be multiple mechanisms depending on circumstance. The mechanism of deoxygenation is different from that of disproportionation since the authors who investigated the reaction for aromatic sulfoxides have consistently reported that sulfone is not observed.

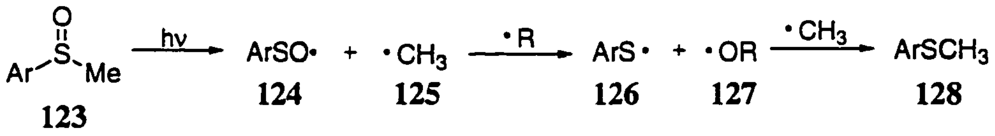
Two mechanisms were proposed in the early literature to account for sulfoxide deoxygenation. The first one is a dimer mechanism that was suggested nearly simultaneously by Shelton[41] and Posner.[47] It is outlined for a generic sulfoxide below.



122

The dimer **122** that contains an O-O bond was formed when the excited sulfoxide triplet is trapped by another ground state sulfoxide molecule. Even though Posner was not specific about the structure of a dimer or other intermediates, he suggested that singlet molecular oxygen, $^1O_2$ ($^1\Delta_g$) is produced in this reaction. In Shelton's mechanism, the formation of ground state oxygen was assumed.

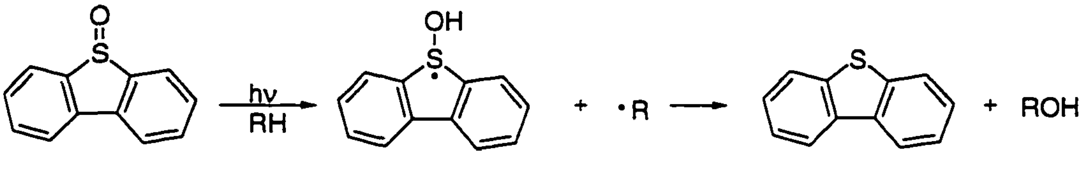
The second mechanism, referred to here as the sulfinyl mechanism,[25] was suggested in the early 1980s on the basis of CIDNP study of the photochemistry of aryl methyl sulfoxides.[15,48] It is shown below. The key step is the reaction between a free sulfinyl radical (formed by α-cleavage) and another radical to effect oxygen atom transfer.



123 **124** **125** **126** **127** **128**

The sulfinyl mechanism can now be ruled out. First, the SO bond in a sulfinyl radical is very strong. Using Benson's estimate for the heat of formation of the phenyl sulfinyl radical (13 kcal/mol)[42] and standard values for the other relevant compounds,[49] the S-O bond energy is ca. 102 kcal/mol, whereas the C-S bond is 35 kcal/mol weaker. Second, transfer of oxygen atom from phenyl sulfinyl to a methyl radical is endothermic by 11 kcal/mol and to epoxidize ethylene with benzenesulfinyl radical is endothermic by 40 kcal/mol. Finally, from the α-cleavage work reviewed previously, it is clear that the reaction of an arenesulfinyl radical with a carbon radical produces a sulfenic ester or disproportionation product.

Two other mechanisms have been investigated by the Jenks laboratory, but all of the work has been on dibenzothiophene sulfoxide **129**.[50,51] First mechanism is that the sulfoxide undergoes hydrogen abstraction, followed by hydroxyl transfer by **130** to the resultant solvent radical.



129 **130** **131**

The other mechanism is proposed in which the sulfoxide cleaves off an oxygen atom directly out of the excited state.[51] The sulfide is produced immediately. Since the O atom and sulfide exist in a solvent cage, there will be competition between geminate recombination and escape of the oxygen atom from the cage. Solvent oxidizing products were isolated. It is the latter mechanism that finds support in the experimental data.

1.3.4 Stereomutation

Stereomutation is one of the most interesting photoreactions of sulfoxides. As described previously in this chapter, sulfoxides with two different substituent groups are chiral molecules, since sulfur atom has four different substituents, oxygen, two different organic groups, and lone-pair electron. Its chirality and ease of preparation makes sulfoxide a chiral auxiliary as an useful synthetic route. The term "racemization" represents the stereomutation in the absence of other stereogenic sites. However, stereomutation can also occur in the presence of other stereogenic sites, leading to diastereomers.[52] Specific details of stereomutation of sulfoxides are described in section 1.4 in this chapter.

1.4 Stereomutation of sulfoxides

Stereomutation of sulfoxides is reviewed here with three subcategories: thermal, photochemical, and chemical stereomutation.

1.4.1 Thermal stereomutation

The first stereomutation of sulfoxides was reported by Krafft and Lyons[53] more than 100 years ago. It was thermal racemization. Not until 1960 was any systematic investigation of mechanism of this process carried out.[54] Based on activation data, there were three different mechanisms for thermal racemization proposed: pyramidal inversion (Figure

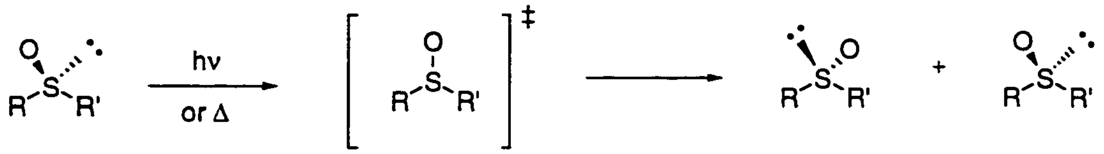


Figure 10. Stereomutation by the pyramidal inversion mechanism.

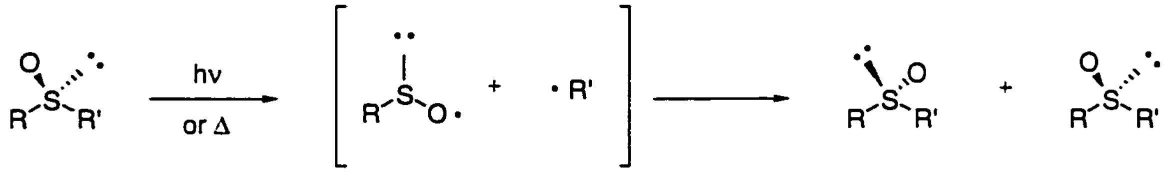


Figure 11. Stereomutation by the α-cleavage mechanism.

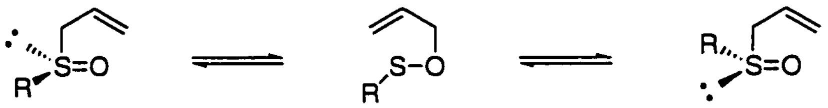


Figure 12. Stereomutation by cyclic rearrangement.

10),[55,56] α-cleavage (Figure 11),[1,57] and cyclic rearrangement (Figure 12).[57-59] The structure of the sulfoxide determined which was predominant.

For pyramidal inversion mechanism, the rate constants for racemization are relatively insensitive to the structure of the carbon substituents at sulfur.[55] The first order rate constant of racemization is about 3×10^{-5} s^{-1} in *p*-xylene at 210 °C for all diaryl sulfoxides and for some aryl alkyl sulfoxides. With various substituents, it remained within one order of magnitude of that value. The activation parameters were in narrow ranges: $\Delta H^{\ddagger}$ 35 to 42 kcal/mol, and $\Delta S^{\ddagger}$ -8 to +4 e.u.

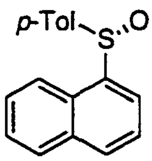
Pyramidal inversion of sulfoxides occurred at the relatively high temperature range between 190-220 °C. Benzyl *p*-tolyl sulfoxide however, racemized in benzene or *p*-xylene in a much lower temperature range (130-150 °C).[1,57] This was attributed to thermal α-cleavage, much as previously described for photochemistry. Racemization occurred with extensive decomposition. Two main decomposition products were dibenzyl and *p*-tolyl *p*-toluenethiosulfonate, which are escape products of radicals. Another piece of evidence is that a much higher positive entropy of activation (+25 e.u.) was obtained for this process.

The cyclic rearrangement mechanism was suggested for allyl sulfoxides.[54,59] Even though the bond dissociation energies of benzyl ($PhCH_2$-X) and allyl compounds (CH_2=$CHCH_2$-X) are very similar,[60,61] the racemization reaction of allyl sulfoxide occurred at a much lower temperature range (50-70 °C) than benzyl sulfoxide. Also, unlike benzylic sulfoxide system, no significant decomposition products were observed.

1.4.2 Photochemical stereomutation

The mechanisms for photochemical stereomutation of sulfoxides were begun to be investigated at 1960s. Like thermal racemization, both α-cleavage and direct pyramidal inversion have been invoked.[1,25,62]

The first examples of photoinduced racemization of sulfoxides were demonstrated by Mislow and his co-workers in 1965.[52] Direct irradiation of nitrogen purged (-)-(*S*)-α-naphthyl *p*-tolyl sulfoxides solution through a 285 nm cut-off filter yielded completely racemized sulfoxides (70% isolated yield) and gave other unidentified products.[52] The use of naphthalene as a photosensitizer provided a higher yield of racemization than did direct irradiation. Also, intramolecular sensitization yielded higher efficiency than intermolecular cases. Unlike the diaryl or alkyl aryl sulfoxides cases, no detectable racemization was observed for dialkyl sulfoxides under their conditions. As an extension of this study to *cis-trans* isomerization, only cis isomer was isolated from the direct irradiation of either *cis-* or *trans*-thianthrene-*S*, *S'*-dioxide **133**.



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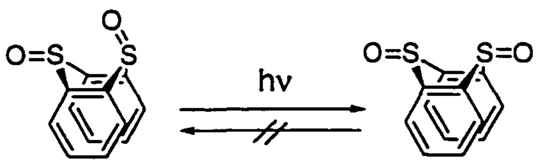
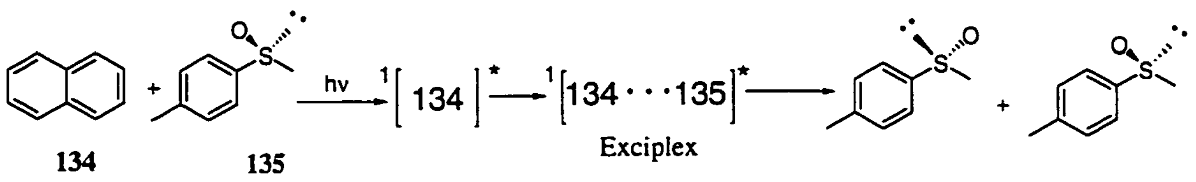
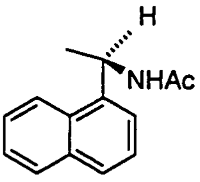


trans-**133** *cis*-**133**

The mechanism of naphthalene sensitized stereomutation of *para*-substituted phenyl methyl sulfoxides under photochemical reaction condition was studied by Cooke and Hammond.[63] Since both the singlet and the triplet energies of naphthalene were lower than the respective state energies of sulfoxides, exciplex formation between naphthalene and sulfoxide was suggested.[63,64] Based on the sensitization experiments the authors concluded that not triplet but singlet excited state of naphthalene was involved in the exciplex formation. No dependence, however, of the quenching rate constants was shown with various electron donating and withdrawing groups on para position of benzene ring of sulfoxides. No steric effect on the rate constants was obtained, either. Neither was the spectroscopic evidence for the formation of exciplex. An exciplex and/or electron transfer hypothesis was supported from the research done by the Jenks group in 1996.[65] The details will be covered in Chapter 3 in this dissertation.

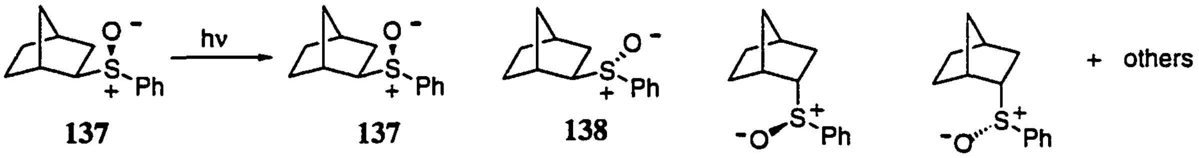


As an example of photoinduced partial optical resolution of a sulfoxide based on the stereomutation reaction, Kagan and his colleague provided a second stereogenic center externally by using a chiral naphthalene derivative, **136**, as a photosensitizer and accomplished modest enantiomeric excess from the irradiation of (S)-*p*-tolyl methyl sulfoxide to (R)- *p*-tolyl methyl sulfoxide.[66]



(R)-**136**

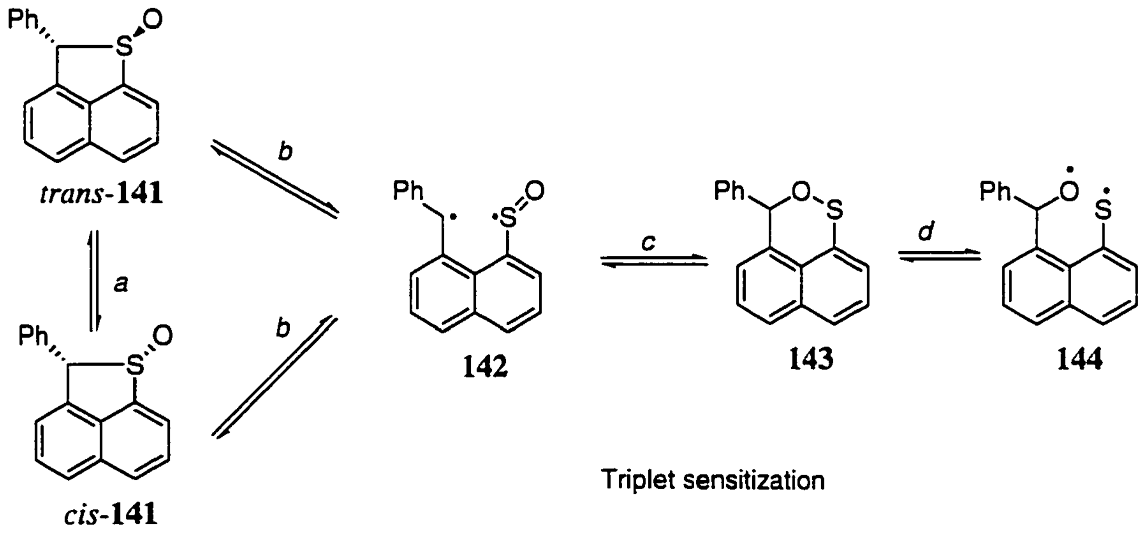
Kropp et al provided a unimolecular case through radical formation.[67] Photolysis of $(2R^*,R^*_S)$-2-norbornyl phenyl sulfoxide **137** yielded approximately 0.7:1 photostationary state mixture of **137** and **138** with other various products. Two other important competing epimerized products **139** and **140** in this literature were detected in low yields.



137 **137** **138** **139** **140**

The products **139** and **140** from **137** in the above reaction clearly provided strong evidence for the bond cleavage between sulfur and carbon, followed by recombination of the radicals. This is an α-cleavage mechanism. The primacy of **137** and **138** could be due to a non-cleavage pathway or to diastereomeric preference for these compounds.

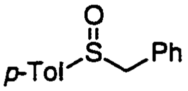
In 1970, Schultz and Schlessinger investigated the role of sulfenate esters in sulfoxide racemization reaction and proposed that pyramidal inversion was the predominant mechanism, though his results did not require it.[68] He suggested pyramidal inversion could occur with little or no barrier in the excited state prior to the internal conversion down to the ground state.[68]



Triplet sensitization

Sensitized photolysis of *trans*- or *cis*-**141** at 366 nm gave a 1:4 photostationary state between the two, while different quantum yields were obtained, 0.70 for trans-**141** and 0.18 *cis*-**141**. Prolonged sensitized photolysis allowed observation of a small quantity of sultene **143**. He proposed that the majority of the photoracemization occurred through simple pyramidal inversion (path *a*). However this result appears to require that some portion of racemization occurred by α-cleavage between sulfur and carbon atom to form biradical **142** (path *b*). Furthermore, α-cleavage could account for all of the stereomutation. Interestingly, C-O homolysis (path *c*) of the sultene was observed when it was photolyzed in the presence of a triplet sensitizer. Though S-O bond cleavage (path *d*) is common, no C-O homolysis has been reported in other cases.

Supporting evidence for the existence of pyramidal inversion mechanism was provided by Guo and Jenks in 1997, in the form of the quantum yields for loss of optical activity and for loss of starting material for compounds **145**, **146**, and **147**.[34] For compound **145**, which has a high quantum yield for formation of benzyl and aryl sulfinyl radicals, the quantum yield of loss of optical rotation (0.4) is as twice great as the quantum yield loss of starting material (0.2). For compounds **146** and **147**, which have lower quantum yields for chemical reaction or observation of arenesulfinyl radical, the quantum yield of loss of optical



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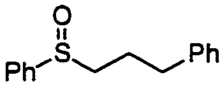

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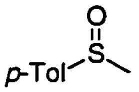
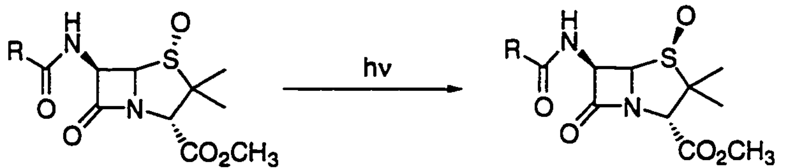


147

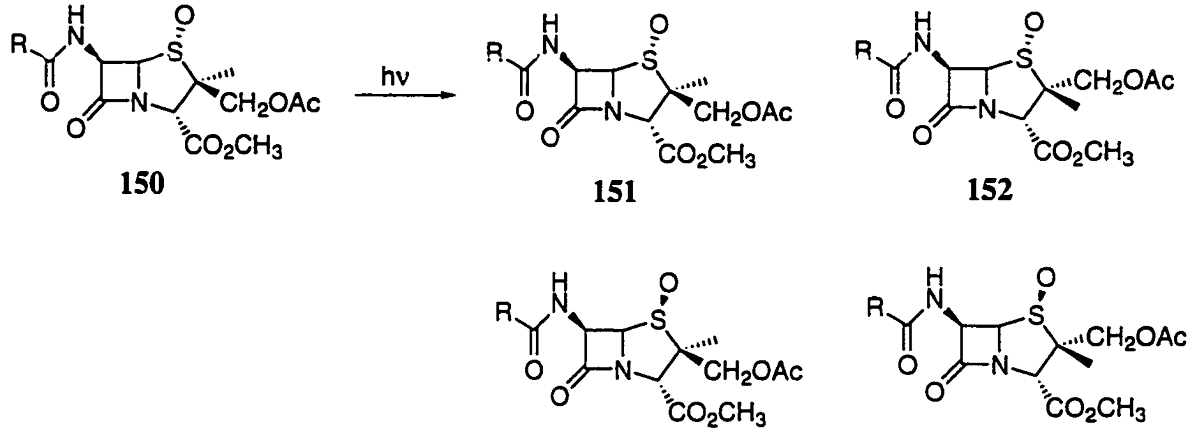
	145	146	147
Φ(loss of optical rotation)	0.42	0.81	0.83
Φ(loss of starting material)	0.21	0.04	0.40

rotation is 20 times higher than the quantum yield loss of starting material. This implicates the involvement of pyramidal inversion.

All of the previous examples are photoracemization of diaryl or aryl alkyl sulfoxides. A few examples of dialkyl sulfoxides stereomutation were reported. In 1969, Archer and DeMarco prepared penicillin (R)-sulfoxides **149** from penicillin (S)-sulfoxides **148** by photolysis in acetone.[69] Oxidation of sulfides or chemical inversion of the (S)-sulfoxides by using the trimethyloxonium fluoroborate methods[70] failed to produce compound **149**. In this stereomutation, it is uncertain whether the α-cleavage mechanism is involved or not. The photolysis of slightly modified compound **150** under identical conditions gave all four possible diastereomers, which implied the cleavage between sulfur atom and tertiary carbon center.[71].

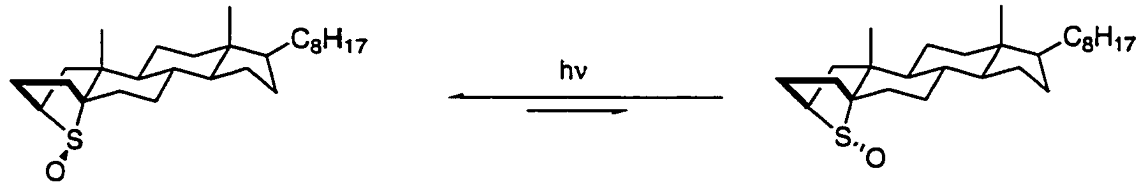


148 **149**

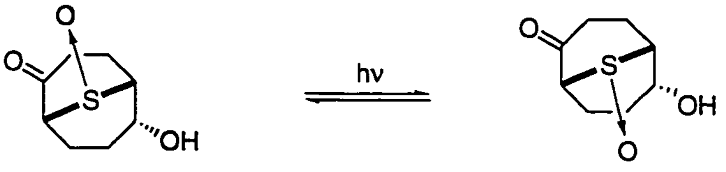


150 **151** **152** **153** **154**

In 1971, Kishi and Komeno reported an example of non-sensitized photoisomerization of a dialkyl sulfoxide.[72] Direct photolysis of **155** gave a 9:1 ratio of **155** and **156**, whereas direct irradiation of **156** gave a 77:23 ratio of **155** and **156**. Longer irradiation did not change the ratio, but more decomposition was observed due to an additional photochemical reaction. No mechanism was proven for this photoracemization.



155 **156**



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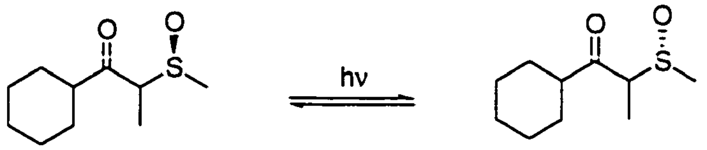

159 160

In 1971, Ganter and Moser reported photoinduced inversion of saturated β-ketosulfoxides **157**, **158**, **159**, and **160** resulting from (C_α-S)-cleavage.[73] Also, a mechanism, which explained photoracemization by a intramolecular energy transfer from the excited state of the carbonyl, was suggested. A more likely mechanism is simple β-cleavage of the ketone.

Finally, photoracemization reactions in solution of chiral diaryl sulfoxides with various aromatic rings were investigated by Tsurutani et al.[62] Experimentally, their results are similar to the earlier results of Guo and Jenks.[34] Based on simplified MO calculations and fluorescence measurements, they asserted that photoinversion occurred when electronic states change from n-σ^* states to the ground state.

1.4.3 Acid-catalyzed racemization

The stereomutation of sulfoxides has been induced by a variety of chemical reagents, such as acids (HCl, H_2SO_4, HI, HF, trifluoroacetic acid and phosphoric acid), acetic anhydride, nitrogen tetraoxide, and potassium *t*-butoxide.[1,74] Among them, the HCl reaction has been extensively investigated.[1,75,76] The prototypical stereomutation of sulfoxide by HCl is depicted in Figure 13. The structure of sulfodichloride was known to be a distorted trigonal bipyramid with chlorine atoms located at apical positions.

$$R_1R_2SO + HCl \rightleftharpoons R_1R_2\overset{+}{S}OH\ \overset{-}{Cl} \rightleftharpoons R_1R_2S(OH)Cl$$

$$R_1R_2S(OH)Cl + HCl \rightleftharpoons [R_1R_2S(OH_2)Cl]^{+}\ Cl^{-} \rightleftharpoons R_1R_2SCl_2 + H_2O$$

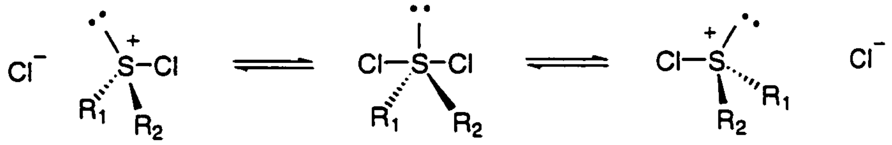

Figure 13. Stereomutation by HCl.

1.5 Summary

Throughout the chapter, photochemistry of sulfoxides in the literature is reviewed. It provides background to understand sulfoxide photochemistry, even though many fundamental questions remain unanswered. α-Cleavage is the most cited process in the literature and well established in a number of reactions, for instance, but nothing is known about the rates of these reactions. The role of hydrogen abstraction as a primary photochemical process is questionable. Along with α-cleavage/radical recombination mechanism, direct pyramidal inversion is a strong possibility as a mechanism of stereomutation, but not well established.

Again, this dissertation focuses on obtaining the photophysical properties of sulfoxides and finding out the relationship between photophysics and stereomutation of sulfoxides. It will unveil an aspect of sulfoxide photochemistry and provide a better understanding of sulfoxide photochemistry in the end.

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CHAPTER II

PHOTOCHEMISTRY AND PHOTOPHYSICS OF AROMATIC SULFOXIDES: CHARACTERIZATION OF THE TRIPLETS AT CRYOGENIC TEMPERATURES

Based on a paper published in the *Journal of Physical Chemistry*[1]

William S. Jenks, Woojae Lee, and David Shutters

Abstract: Aromatic sulfoxides are photochemically active molecules. Much of that reactivity has been attributed to the triplet states of these molecules. At 77 K in ether/isopentane/ethanol (EPA) glass, aromatic sulfoxides are shown to have weak phosphorescence. The triplet energies are a few kilocalories per mole higher than the corresponding ketones. The diaryl sulfoxides are about 3 kcal/mol lower than the corresponding ketones, and the diaryl sulfoxides are about 3 kcal/mol lower than the corresponding aryl methyl sulfoxides. For instance the triplet energy of diphenyl sulfoxide is 78 kcal/mol, whereas the triplet energy of methyl phenyl sulfoxide is estimated to be 81 kcal/mol. The lifetimes of emission are generally under 100 ms. From the diffuse

vibrational structure of the spectra, the lifetimes, and the effect of solvent on the triplet energy, it is concluded that the triplets are delocalized aromatic states that involve substantial charge transfer off the oxygen atom.

2.1 Introduction

The sulfoxide functional group is extensively used as a synthetic intermediate and chiral auxiliary, and further elaboration of this chemistry is the subject of substantial continuing effort.[2-9] Sulfoxides are also known to undergo photochemical reactions of several types,[10-13] but this chemistry has not been developed or generalized in parallel fashion. Recently, various characteristics of photochemistry of sulfoxides were systematically reviewed by Jenks group.[14]

As the foundation of a systematic study of the photochemistry and photophysics of aromatic sulfoxides, the lowest triplets of a set of aryl alkyl and diaryl sulfoxides have been characterized by studying their emission characteristics in organic glasses at 77 K. In addition, the result for several sulfoxides is compared to the corresponding sulfides and sulfones. We also discuss time resolved electron paramagnetic resonance (TREPR) spectra obtained at 15 K for several of these compounds.

The class of photochemical reactions of sulfoxides that has been best documented involves cleavage of the S-C bond (α-cleavage) and yields products derived from the resulting radical pair or biradical. Strongly supporting the α-cleavage mechanism is the observation by steady-state EPR of the sulfinyl radicals themselves and their spin-trapping products.[15-17] Products rationalized by a mechanism involving α-cleavage include racemates of starting material, sulfenic esters (R-S-O-R') and their photoproducts, products representing loss of SO, and other radical recombination and disproportionation products.[18,19] Several reaction products have been rationalized on the basis of hydrogen abstraction by the oxygen atom, but there is no direct evidence supporting the mechanism. A third class of reaction is the photodeoxygenation of sulfoxides to sulfides.[20]

In most cases, where an assignment has been made in the early literature, the photoreactivities of aromatic sulfoxides have been attributed to their triplet states.[11,21-31] These assignments have generally been made using the ordinary criteria of triplet sensitization and quenching experiments. While characterization of the triplet states of ketones has played a critical role in the development of their photochemistry, the same cannot be said for sulfoxides. Previous to this work, there were only three reports of phosphorescence from aromatic sulfoxides,[30,32,33] no quantum yields or lifetimes, and no qualitative characterizations. Moreover, the little information that exists casts serious doubts that sensitization by relatively low energy molecules such as benzophenone and naphthalene is by the standard energy-transfer mechanism.[21-25,30,31,34] In this dissertation, it is shown that although the excitation of aromatic sulfoxides is not localized on the SO chromophore, the sulfinyl substitution is critically important to the nature of the lowest aromatic triplet. Phosphorescence at 77 K is typically an inefficient process for the sulfoxides we examined, and the triplet lifetimes we could measure are generally in the range of 35-100 ms. The triplet energies of sulfoxides are between those of the corresponding ketones and the unsubstituted aromatics. We also show that the charge density on the sulfoxide oxygen is substantially reduced in the triplet state.

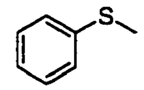
2.2 Results

Compounds.

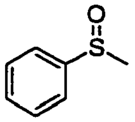
We chose to study compounds of two general classes: symmetrical diaryl sulfoxides and aryl methyl sulfoxides. We chose symmetrical diaryl sulfoxides in order to avoid localization of excitation on the low-energy "half" of the molecule. In addition, we examined the luminescence of several of the corresponding sulfides and sulfones. These compounds used in the study are illustrated in Figure 1.

Emission Spectra and Spectroscopic Excitation Energies.

None of the sulfoxides examined exhibited any luminescence at room temperature in a variety of solvents. There is one report of fluorescence from **1-SO**,[35] which we were not



1-S



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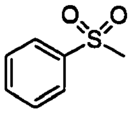

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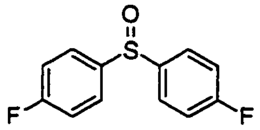
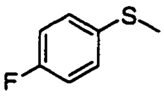


11-SO



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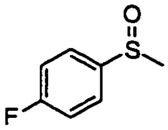

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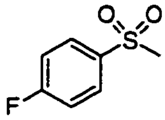

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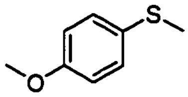

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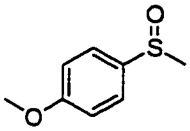

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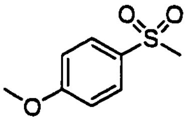

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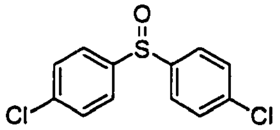
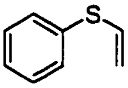
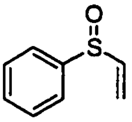


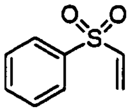
12-SO



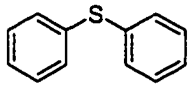
4-S



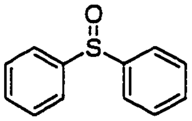
4-SO



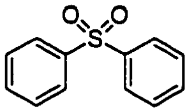
4-SO$_2$



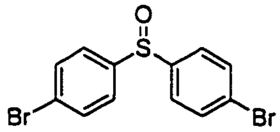
5-S



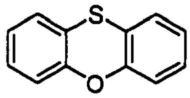
5-SO



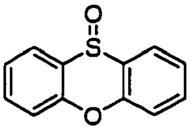
5-SO$_2$



13-SO



6-S



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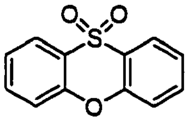

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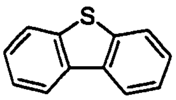
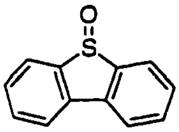
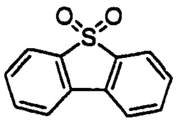


7-S



7-SO



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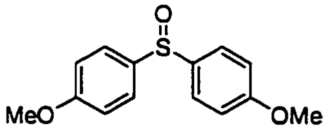
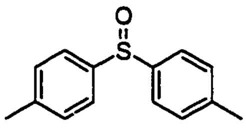
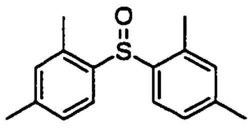


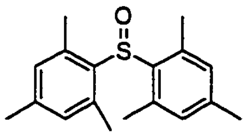
14-SO



8-SO



9-SO



10-SO

Figure 1. Compounds used in the present study.

able to reproduce. It is likely that the reported fluorescence was from am impurity, most likely **1-S**, *vide infra.*

At 77 K, however, phosphorescence was observed from most of the compounds and fluorescence from a few. The luminescence of all the compounds were examined in 5:5:2 ethyl ether:isopentane:ethanol (EPA) glass. The sulfoxides were substantially more soluble in this mixture than in any of the standard hydrocarbons used for organic glass. We were unable to completely strip 2-methyltetrahydrofuran of aromatic impurities that made its use impractical for many of the sulfoxides, which do not have substantial absorption coefficients beyond about 275 nm.

Fluorescence.

Among the sulfoxides, fluorescence at 77 K was observed only from three compounds: **3-SO**, **6-SO**, and **7-SO**. The singlet energies are listed in Table 1. In each case, the fluorescence was a relatively minor part of the luminescence, perhaps no more than 10% of the total. The fluorescence of **7-SO**, which was nonexponential but in the nanosecond regime, showed that the fluorescence was prompt. The millisecond lifetime (*vide infra*) of the phosphorescence and large energy gap between the fluorescence and the phosphorescence made delayed fluorescence an unreasonable explanation.

Table 1. Spectroscopic singlet energies for those sulfoxides which showed fluorescence at 77 K in EPA.

Compound	Singlet Excitation Energy (kcal/mol)
3-SO	99
6-SO	91
7-SO	85

Triplet Energies.

The phosphorescence spectra of most of the sulfoxides were very similar in appearance. The spectrum obtained from ditolyl sulfoxide, which is typical, is presented inFigure 2. There is a single shoulder on the high-energy side and then a relatively unstructured band. The triplet energies that appear in Table 2 are taken from the λ_{max} of the blue edge band. The principal variation among the phosphorescences of the sulfoxides is whether any additional (broad) structure is visible and the width of the band. Only the two tricyclic sulfoxides, 6-SO and 7-SO, showed any complex vibrational structure. Weak S to T_1 excitation spectra were observed for a few of the sulfoxides; no large Stokes shifts were found.

Again with the exception of the dibenzothiophene (**7**) system, all of the sulfides have triplet energies lower than the corresponding sulfoxides. The triplet energies of the sulfones are typically comparable to, but a little higher than, those of the sulfoxides. Figure 3 illustrates the spectra of diphenyl sulfide, sulfoxide, and sulfone (**5-S**, **-SO**, and **-SO$_2$**).

The spectroscopic triplet energies of aryl methyl sulfoxides (**2-SO** and **3-SO**) are 78 and 80 kcal/mol respectively, which is 3 kcal/mol higher than the corresponding diaryl sulfoxides (**11-SO** and **14-SO**). No experimental triplet energies are given for **1-SO** or **4-SO**.

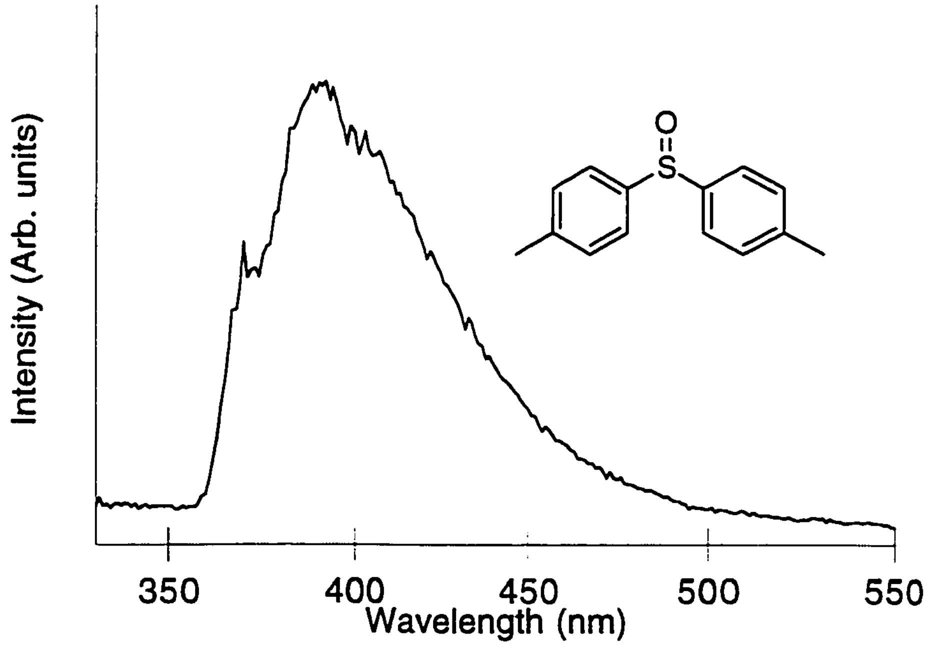


Figure 2. Phosphorescence spectrum of di-*p*-tolyl sulfoxide (**8-SO**) at 77 K in EPA.

Table 2. Spectroscopic triplet energies for all of the compounds which showed measurable phosphorescence at 77 K in EPA glass.

Compound	Triplet Energy (kcal/mol)		
Family	Sulfide	Sulfoxide	Sulfone
1	73[a]	(81)[b, c]	82
2	75	78	81
3	73	80	75
4	75	*b*	*d*
5	73	78	80
6	66[e]	79	79
7	70	61	64
8		77	
9		76	
10		76	
11		75	
12		76	
13		76	
14		77	

[a] 74 kcal/mol in EPA at 77K.[36] [b] Emission from these sulfoxides was very weak or non-existent. No spectrum, however weak, that differed from that of the corresponding sulfide could be obtained. [c] Triplet energy estimated to be 81 kcal/mol. [d] Emission too weak to obtain a triplet energy. [e] In agreement with literature reports in ethanol glass.[33,37]

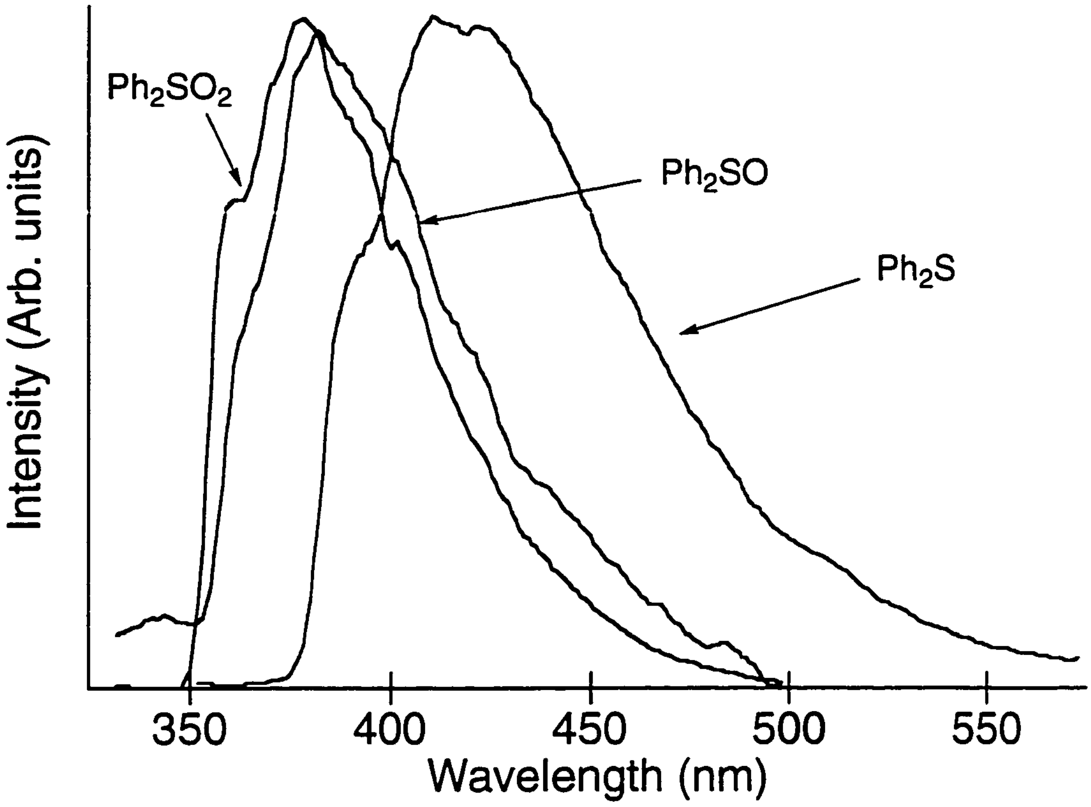


Figure 3. Phosphorescence spectra of **5-SO$_2$**, **5-SO**, and **5-S** (diphenyl sulfone, sulfoxide and sulfide) at 77 K in EPA. The spectra have been normalized for presentation.

Only extremely weak spectra could be obtained from these compounds, and they were indistinguishable from those obtained from the corresponding sulfide. We estimate the triplet energy of phenyl methyl sulfoxide, **1-SO**, to be 81 kcal/mol, based on the three following criteria: (1) The known triplet energy of *p*-bromophenyl methyl sulfoxide, **15-SO**, is 79 kcal/mol;[30] (2) the triplet energy of diphenyl sulfoxide, **5-SO**, is 2 kcal/mol higher than the corresponding bromo substituted compound, **13-SO**; and (3) the 3 kcal/mol correlation between the diaryl and aryl methyl sulfoxides places the triplet energy of **1-SO** at 81 kcal/mol. We are unable to estimate the triplet energy of **4-SO** with any specificity.

Solvent Effects on Triplet Energies.

The sulfoxides with significant phosphorescence in EPA were also examined in methylcyclohexane (MCH), along with their corresponding sulfides and sulfones. The triplet energies of these compounds are shown in Table 3. Those of the sulfides were essentially insensitive of the solvent change. Sulfones showed only a small sensitivity, approximately -1 kcal/mol, whereas most of the sulfoxides showed solvent shifts, from -3 to -10 kcal/mol. The direction of the shift, from larger triplet energies in the more polar solvent to smaller triplet energies in the nonpolar solvent, implies that the triplet state of the sulfoxide is less polar than the ground state. The spectra of the sulfoxides are of the same general appearance as in EPA, but the shoulder on the blue edge is generally less pronounced. Benzophenone is included in Table 3 for reference.

Table 3. Triplet energies[a] in EPA and methylcyclohexane (MCH), with energy shift.

	Sulfides			**Sulfoxides**			**Sulfones**		
Family	**EPA**	**MCH**	**ΔE_T**	**EPA**	**MCH**	**ΔE_T**	**EPA**	**MCH**	**ΔE_T**
3	73	72	-1	80	75	-5	75	74	-1
5	73	73	0	78	*b*		80	79	-1
6	66	66[c]	0	79	69	-10	79	74	-5
7	70	70	0	61	58	-3	64	64	0
8				77	72	-5			
9				76	71	-5			
11				75	68	-7			
12				76	75	-1			
13				76	73	-3			
14				77	74	-3			
Benzophenone	69.4	68.4	-1						

[a] All energies in kilocalories per mol.

[b] Too weak to obtain a spectrum

[c] 65 kcal/mol in isopentane.[38]

Quantum Yields.

Another fundamental difference between the phosphorescence of the sulfides and sulfoxides is the intensity of emission. The quantum yields of phosphorescence are shown in Table 4. There are a few compounds which have triplet energies listed in Table 3 but only an upper limit on the quantum yield in Table 4. This is because more concentrated solutions (*ca.* 1 mM) were used for the triplet energy determinations, but optically dilute samples (absorbance ≤ 0.1 in the 5-mm cell, concentrations 10^{-4}-10^{-5} M) were used for the quantum yields. Under these conditions, good spectra for integration could not be obtained.

Lifetimes.

Data for none of the sulfoxides (save the long-lived **6-SO**) and very few of the other samples with lifetimes under about 200 ms could be satisfactorily fit to single-exponential decays. Since there was no physical basis for attributing discreet numbers lifetimes to these samples frozen in organic glasses, fits were obtained using a distribution of exponentials routine.[42] Benzophenone, under identical experimental conditions, yielded a decay that was best described by a distribution of lifetimes about a central value of 5 ms. It must also be noted that it is because the data are of particularly high quality that the deviations from single exponentials are even observed from some of the samples. Data sets fit to distributions of exponentials had at least 100,000 counts in the peak data channel.

Table 4. Quantum yields of phosphorescence at 77 K in EPA

Compound	**Phosphorescence quantum yield**[a]		
Family	**Sulfide**	**Sulfoxide**	**Sulfone**
1	0.32	<0.001	0.15
2	0.25	~0.001	0.033
3	0.15	0.018	0.35
4	0.041	<0.001	<0.001
5	0.45	≤0.004	0.54
6	0.84[b]	0.014	0.53
7	0.47[c]	0.040	0.075
8		0.053	
9		0.007	
10		≤0.003	
11		0.010	
12		0.031	
13		0.061	
14		0.10	

[a] Benzophenone ($\Phi_{Ph} = 0.74$)[39] was used as a standard.

[b] $\Phi_{Ph} = 0.64$ in cyclohexane at 77 K.[40]

[c] In agreement with literature value of 0.47 in ethanol glass.[41]

The lifetimes listed in Table 5 include an error limit which is associated with the "band width" of the distribution. Often, more than one "band" would appear as a result of the fit. A decision on whether to report the lifetime as the center of the most important band or to simply label it as polyexponential was made in the following way:

The fraction of photons attributable to component l in a decay described by a sum of exponentials is given by

$$\% \text{ from component } l = A_l \tau_l \, / \sum A_j \tau_j \qquad (1)$$

where A_j is the pre-exponential factor and τ_j is the lifetime of that exponential. Using this equation, we can crudely estimate the contributions of different bands within a distribution fit. If a single band did not contribute more than 90% of the photons for that decay (as estimated by eq 1), the lifetime is listed as "multiexponential" in Table 5. In some cases, an artifactual component with small pre-exponential factor and long lifetime (≥ 0.5s) was ignored. These artifacts, we believe, are the result of the data being collected at a 1-Hz rate, rather than allowing the samples to completely decay between pulses.

Table 5. Phosphorescence lifetimes at 77K in EPA.

Compound	**Lifetime[a] (ms)**		
Family	**Sulfide**	**Sulfoxide**	**Sulfone**
1	22 ± 6	*b*	~600[c]
2	34 ± 18	*b*	300
3	*d*	*d*	~530
5	20 ± 6	*d*	~1100[c]
6	90 ± 26[e]	~600[c]	~720
7	~1300[c,f]	80 ± 20	85[g]
8		66 ± 29	
9		*e*	
10		*b*	
11		*d*	
12		35 ± 9	
13		1.9 ± 0.6	
14		102 ± 36	

[a] Unless otherwise noted, data yielding lifetimes under 200 ms were fitted to a distribution of exponentials. Errors listed are the standard deviations of the components within a given lifetime band. [b] Too little phosphorescence was observed to measure a lifetime. [c] Accuracy of lifetime limited by the minimum pulsing rate, 1 Hz. [d] Polyexponential, but all components ≤100 ms. [e] 72 ms in cyclohexane[40] and 0.07 s in isopentane.[38] [f] In agreement with literature value of 1.5 s,[41] 1.45 s,[43] and 1.3 s[44] in ethanol glass. [g] Monoexponential.

EPR.

EPR data were obtained to derive the zero field splitting parameters, from which conclusions might be drawn about the localization (or lack thereof) of the excited state. Another question we hoped to address at least indirectly was whether the low phosphorescence yields were due to fast nonradiative decay of the triplets or a low triplet yield, since very strong sulfoxide signals could imply the former. We first attempted these EPR measurements using the standard technique of irradiating a sample at 77 K (using a high-pressure mercury lamp) in the cavity of an X-band spectrometer with field modulation and continuous detection.[45] After observation of signals from naphthalene and **7-S**, we were unable to detect a signal from any sulfoxide, despite literature reports[33,46] of the triplet EPR of **7-SO** obtained under almost identical conditions.

We now believe this report to be in error for the following reasons: (1) The reported zero field splitting parameters for dibenzothiophene S-oxide (**7-SO**) and dibenzothiophene (**7-S**) are identical; (2) the decays of the $\Delta m = 2$ signal for both compounds are nearly identical, at 2.0 and 1.8 s; and (3) **7-SO** is not photostable, even at 77 K. It converts to **7-S**.[20,47] From Table 5, it can be seen that the phosphorescence lifetime of **7-S** is 1.3 s and that of **7-SO** is 80 ± 20 ms. It is thus not reasonable to observe a 2-S decay of the $\Delta m = 2$ transition for **7-SO**, but it is reasonable for **7-S**. Moreover, minor impurities of **7-S** in **7-SO** would result in spectral contributions much larger than their molar fraction because of the higher steady-state concentration of the longer lived triplet.

We thus resorted to time-resolved EPR methods at 15 K. Because of the lower temperature, we expected lower photoconversion and stronger signals. Because the sample is excited by excimer laser pulse, detection can be carried out for times as short 1 μs beginning only 1 μs after the pulse. This amount of time is clearly orders of magnitude lower than the triplet lifetime of any of the compounds under these conditions and removes the steady-state impurity bias seen in the dibenzothiophene samples. Moreover, the experiment allows observation of strongly polarized triplet sublevel populations. The orientations (emissive or absorptive) of both the $\Delta m = 1$ and $\Delta m = 2$ transitions depend directly on the relative populations of the sublevels during the sampling period. This technique has been applied before to the study of both phosphorescent and nonphosphorescent triplets.[48-52]

Three systems were examined by TREPR, the diphenyl (**5**) series, the phenoxathiin (**6**) series, and the dibenzothiophene (**7**) series. The diphenyl series was chosen because it represented the parent system. The other two were chosen because they are relatively rigid and are expected to have limited numbers of different conformations in the glass. It as been consistently observed that molecules with one or more important degrees of conformational freedom (*e.g.* C-S rotation in **5-S** or C-CO in benzophenone) give much broader, less interpretable spectra. This is attributed to variations in *D* and *E* values as a function of conformation. The **6** series and **7** series both absorb well at the excitation wavelength of 308.5 nm, and the tail of the absorption of **5** is sufficient for experiments carried cut at the high concentrations (*ca.* 50 mM) used. For increased solubility, methyltetrahydrofuran was used as solvent.

Good spectra were obtained for six of nine compounds investigated, and they are shown in Figure 4. The data obtained from the EPR spectra are given in Table 6. The most striking feature from the spectra and Table 6 is that the $\Delta m = 2$ and other transitions of the sulfide and sulfones are polarized in opposite phases. Because we only measure differences in sublevel populations, rather than absolute populations, our experiments do not yield the absolute sign of *D*. There are two solutions that can be used to simulate the spectra; they have opposite signs of *D*, but necessarily different populations. However, that *D* is positive has been firmly established for dibenzothiophene by low-temperature optically detected magnetic resonance (ODMR) studies.[53] The emissive or absorptive phases of the signals in Figure 4 reflect the relative populations of the sublevels at the moment of measurement.

As was observed by Baiwir at 77 K in ethanol glass, [33,54] we obtained no spectrum for **7-SO** at 15 K that was distinguishable from the corresponding sulfide, save for a substantially lower signal-to-noise ratio. The same result is observed for **6-SO**.

Table 6. Zero field splitting parameters derived from TREPR data[a]

compounds	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	D^* (cm^{-1}) from $\Delta m = 2$	D^* (cm^{-1}) = $(D^2 + 3E^2)^{1/2}$	$\Delta m = 2$
5-S	0.1034	0.0045	0.104	0.1037	E
5-SO[b]					
5-SO_2[b]					
6-S	0.1360	0.0023	0.140	0.1361	E
6-SO[c]			0.141		E
6-SO_2[c]			0.110		A
7-S[d]	0.1137	0.0006	0.113	0.1137	E
7-SO[e]	0.114	0.010	0.113	0.115	E
7-SO_2[f]	0.1155	0.0031	0.115	0.1155	A

[a] Error estimated at ±2 in last place reported. [b] No spectrum obtained.

[c] Only $\Delta m = 2$ transition observed. [d] $D = 0.1136$ cm^{-1}, $E = 0.0022$ cm^{-1}, $D^* = 0.1136$ in ethanol glass,[33,54,55] $D = 0.1130$ cm^{-1}, $E = 0.0021$ cm^{-1} in diethyl ether at 77 K,[44] $D = 0.1149$ cm^{-1}, $E = 0.0024$ cm^{-1} in *n*-heptane at 1.3 K.[53] [e] Experimentally indistinguishable from spectrum of **7-S**, save for the intensity. See text for discussion. [f] $D = 0.1136$ cm^{-1}, $E = 0.0022$ cm^{-1}, $D^* = 0.1137$ cm^{-1} in ethanol glass.[33]

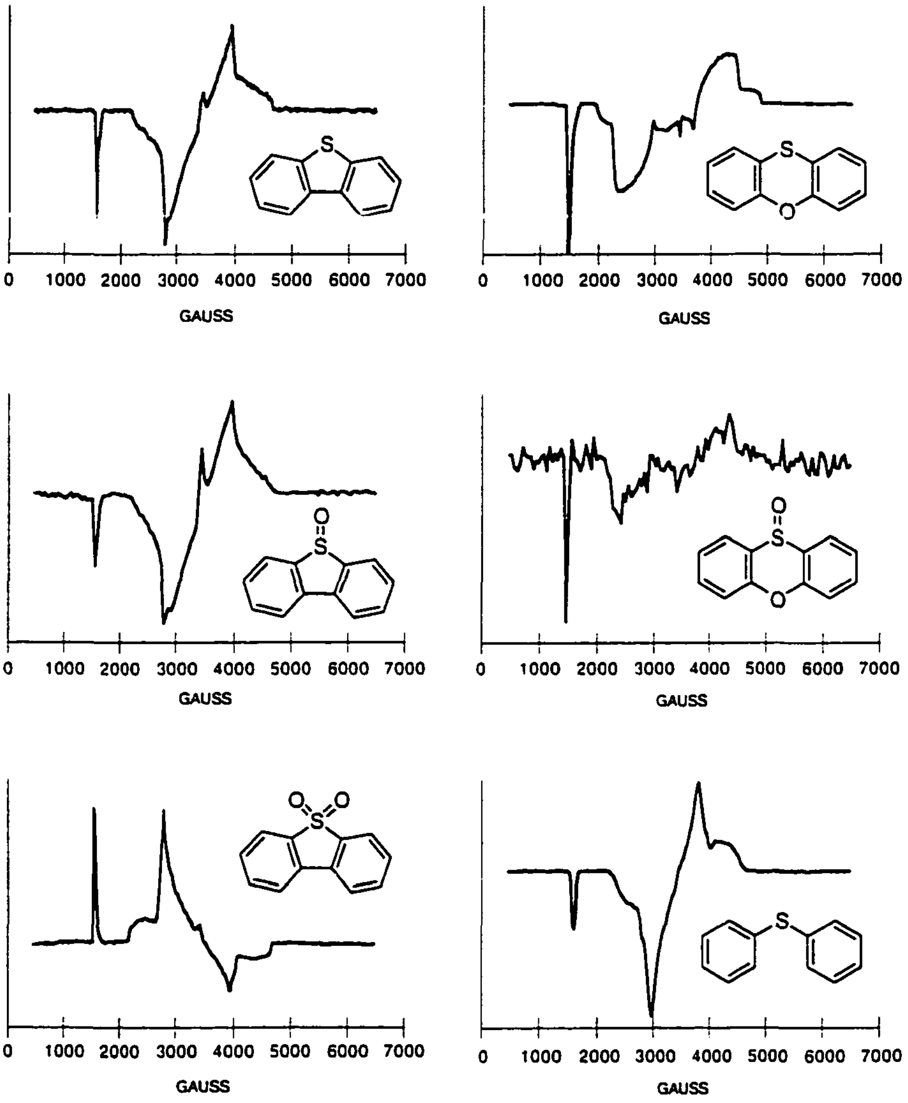


Figure 4. TREPR spectra obtained at 15 K in methyltetrahydrofuran. Excitation was at 308.5 nm, and the detection gate was 1-2 μs after the laser pulse. Spikes observed at about 3400 G are due to radical signals.

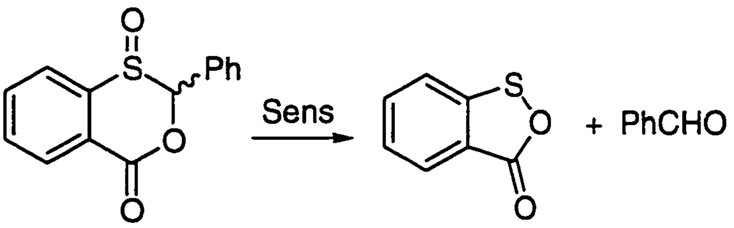
The coincidence of spectra using our technique demands not only identical *D* and *E* values but also identical relative sublevel populations, parameters not available to the previous workers. We believe that this additional constraint on identical spectra reinforces our conclusion that the EPR of triplet dibenzothiophene S-oxide has not yet been observed. We attribute our sulfoxide spectra to small sulfide impurities, either originally present or formed as a result of photolysis of the sample. We also observed a signal, which is not shown, from **6-SO**, but in an ethanol/methanol glass. It had a signal-to-noise ratio intermediate between those shown for **6-S** and **6-SO** in Figure 4 and was superimposable over the spectrum shown for **6-S**.

2.3 Discussion

Excitation energies and implications for sensitization.

The triplet energies of the aromatic sulfoxides are a few kilocalories per mole higher than those of their ketone analogues, and a few kilocalories per mole lower than the corresponding aromatic system without the sulfoxide substitution. It can be said rather generally that benzophenone (E_t = 69 kcal/mol) does not have sufficient triplet energy for efficient energy transfer to simple sulfoxides, unless they have extended aromatic systems, such as **7-SO**. Acetophenone (E_t = 74 kcal/mol) or even acetone (E_t = 82 kcal/mol) would seem to be more appropriate sensitizers when simple triplet energy transfer to sulfoxides is desired for photochemical studies.

Nonetheless, several reports show that photochemical reactions of sulfoxides occur with low-energy sensitizers. Shelton and Davis found that phenyl *tert*-butyl sulfoxide decomposed to give varying mixtures of products attributable to α-cleavage and deoxygenations with sensitizers such as acetophenone, triphenylene (E_t = 66 kcal/mol), and anthraquinone (E_t = 63 kcal/mol).[25] The work of Muszkat and Praefcke shows that C-S cleavage in aryl methyl sulfoxides can be sensitized by benzophenone in cases that seem both reasonable (e.g. biphenyl methyl sulfoxide) and unreasonable (alkoxyphenyl methyl sulfoxides) on the basis of energy transfer.[21-23,25] On the other hand, Lawesson showed that the efficiency of loss of benzaldehyde from 3-phenylthiochloromanone *S*-oxide (**15**) fell off when the sensitizer triplet energy fell as low as about 65 kcal/mol or below.[26] On the basis of the known triplet energy of **16** (58 kcal/mol),[32] which should represent a lower limit of the triplet energy of **15**, and the current data, Lawesson's result probably corresponds to the falloff of energy transfer to **15**. Cooke and Hammond suggested that the racemization of tolyl methyl sulfoxide under naphthalene sensitization might occur via an exciplex.[30] Though the principle is same, they also showed that the singlet state of naphthalene was being quenched by the sulfoxide, and not the triplet.[30] Clearly, further investigations into the sensitization photochemistry of sulfoxides must include consideration of exciplex and/or



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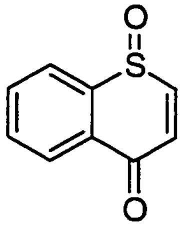

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electron-transfer mechanisms as serious mechanistic alternatives. This will be described in details in Chapter 4.[56]

The deoxygenation problem.

Because of the low luminescence of the sulfoxides and the higher luminescence efficiency of the corresponding sulfides and sulfones, extreme care had to be taken to ensure that we were observing genuine sulfoxide luminescence, particularly with the weakly emitting samples. The photochemical deoxygenation of sulfoxides occurs, in general, without formation of sulfones.[11] We have specifically observed this reaction even at 77 K in EPA glass at concentrations as low as 1 μM for **7-SO**, thus making sulfide luminescence the more serious threat to our measurements.[20]

The case of the diphenyl (**5**) series is illustrative. Both the sulfone and sulfide are about 100 times more phosphorescent than the sulfoxide, so small impurities could easily have been misconstrued for the sulfoxide spectrum. The large red shift of the sulfide made distinction of its spectrum trivial. The sulfone was distinguished by a 5-nm blue shift compared to the sulfoxide and the lifetime measurements. While the decay of diphenyl sulfoxide could not be fit to a single lifetime or even a single-moded distribution of lifetimes, all of the components were under 100 ms. On the other hand, the lifetime of diphenyl sulfone was 1.1 s. No such long component was observed from the samples of **5-SO**, and spectrum was taken to be that of the sulfoxide. Moreover, it was qualitatively observed that spectra obtained as the sample "aged" became more broad, sloping to base line on the low-energy side more slowly. This was taken as an indication that deoxygenation of **5-SO** to **5-S** was occurring and the sulfide was contributing to the spectrum. No spectra that differed from the corresponding sulfides, except by intensity, could be obtained for **1-SO** and **4-SO**. Particularly because we can predict where the energy of **1-SO** should be, which is substantially higher than any observed luminescence, we assigned those spectra to sulfide impurity.

We believe this problem shows up in other experiments as well. As discussed above, we do not believe that the TREPR spectra we obtained for **6-SO** and **7-SO** can be reasonably attributed to the sulfoxides but are rather due to minor sulfide impurities. The nearly exact coincidence of the relative sublevel population rates of **7-S** and **7-SO**, which requires the consonance of two independent parameters, is very unlikely, and reported observation of a 2-s decay time of the signal for **7-SO**[33] when the actual triplet lifetime is about 80 ms would seem to prove this assertion. We also suspect that the reported fluorescence of **1-SO** at room temperature[35] is more likely that of **1-S**, which is known.[36]

Source of the low phosphorescence quantum yields.

The quantum yield of phosphorescence is given by

$$\Phi_P = \Phi_T \ (k_P / [k_P + \sum k_{nr}])$$

where Φ_T is the triplet yield, k_P is the natural phosphorescence rate constants, and Σk_{nr} is the sum of the rate constants of all nonradiative processes of the triplet. Since the fluorescence yields of the sulfoxides are in general quite small, Φ_T could be big in most cases (actual triplet yields of several aromatic sulfoxides were measured and shown in Chapter 3). Thus, the low phosphorescence yields may be accounted for by either low triplet formation yields (Φ_T), relatively fast nonradiative pathways (Σk_{nr}), or a combination of the two. For instance, we observe a substantial heavy atom perturbation for **13-SO**, manifested as an increase in phosphorescence yield and a distinct decrease in phosphorescence lifetime compared to the other compounds. If the sulfoxides triplets, once formed, efficiently emit, the heavy atom effect would be consistent with an increase in triplet yield and phosphorescence rate constant. If, however, the triplet yield is high, but the efficiency of phosphorescence is low, the heavy atom effect could be explained by a larger increase on the phosphorescence rate constant than on the nonradiative decay rate constants.

The TREPR data do not provide a good indication of the triplet yield either. As an example, the phosphorescence yields at 77 K of diphenyl sulfide and sulfone (**5-S** and **5-SO$_2$**) are similar at 0.45 and 0.54. However, at 15 K, an excellent spectrum was obtained for the sulfide and nothing for the sulfone. This is because the intensity of the signal is strongly dependent on the relative sublevel populations in addition to the triplet yield. The triplet yield, relative sublevel population rates, and zero-field splitting parameters may all vary with conformation, possibly worsening the situation.

Because the sum of fluorescence and phosphorescence quantum yields is well below unity for all of the sulfoxides, it is clear there is efficient nonradiative decay from either or both of singlet and triplet manifolds. We cannot yet distinguish between the two. One of the obvious candidate for an efficient nonradiative decay is the photoracemization of sulfoxides. The quantum yields of photochemical racemization of sulfoxides were shown in Chapter 3 on this dissertation and reported by Tsurutani group independently.[57,58] The deoxygenation reaction of **7-SO** has a rather low quantum yield at room temperature, so it is rather unlikely that irreversible chemical reactions are important nonradiative pathways. we cannot, however, rule out a C-S cleavage reaction which is rapidly reversed in the solid matrix. We have observed no sensitization of biacetyl phosphorescence (up to 18 mM) by **7-SO** at room temperature, but even this result may be explained by a short lived triplet, as well as by low triplet yield, since the energy-transfer rate under those conditions should be about 10^8 s^{-1}.[59]

Nature of the sulfoxide triplet states.

The triplet states of simple aromatic sulfoxides are not localized on the sulfoxide functionality but are rather aromatic $\pi\pi^*$-type states that are strongly perturbed by the presence of the sulfoxide. The strength of that perturbation can easily be seen by comparing the results obtained for sets of sulfides, sulfoxides, and sulfones. The diffuse vibrational structure in the phosphorescence spectra pointed to a delocalized aromatic excited state. The triplet lifetimes of roughly 30-600 ms, with all but one ≤100 ms, are a little short for typical $\pi\pi^*$ states. However, other standard criteria point to this conclusion.[60] A strong internal heavy atom perturbation is observed with **13-SO**. The singlet-triplet gap (S_1-T_1), when known, is large: 19, 12, and 21 kcal/mol for **3-SO, 6-SO**, and **7-SO**, respectively. Also, the lack of large Stokes shift between the observed $S_0 \rightarrow T_1$ excitation and phosphorescence spectra implies that there are not large changes in molecular geometry in the triplet state.

Another critical parameter in the characterization of excited states is the change in charge distribution from that of the ground state. This information can be experimentally approached by examining the energy of emission as a function of solvent polarity. In liquids, and particularly with fluorescence, one can measure the change in dipole moment, $\Delta\mu_{ex}$, by examining the absorbance and emission spectra as a function of solvent.[61] Several alternative data treatments are advocated,[62] but they all rest on knowing the refractive index and static dielectric constants of the media involved. Because the static dielectric constant is reflective of the solvent's ability to react to charge by its own motion, these expressions are not valid when the solvent is frozen, as in the present experiments. Observed shifts in the frozen solvents are probably larger than they would be in fluid solvent because of the lack of solvation of the excited state, with its new charge distribution.

However, the observed shifts in triplet energy for the sulfoxides are notable for both their direction and magnitude. The $\pi\pi^*$ excited states of most polar aromatic molecules are stabilized, relative to the ground state, by polar solvents, implying that charge separation is greater in the excited state than in the ground state. This is even true of the great majority of polar "push-pull" aromatic compounds, whose excited singlets are characterized by greater charge transfer then the ground states. For example, *p*-nitroaniline (**17**) and 2-aminonaphthalene-6-sulfonate (ANS, **18**) have $\Delta\mu_{ex}$ values of 15 D[63] and 9 D,[61,64,65]

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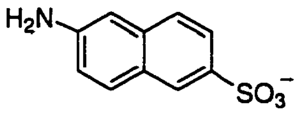

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respectively. Other ANS derivatives have $\Delta\mu_{ex}$values of up to 40 D. The same trend is, of course, observed for triplets which are more polar than the ground states. The phosphorescence spectra of electron-donating substituted acetophenones and **17** (all $^3\pi\pi^*$), for instance, are all red-shifted in polar solvent.[66]

By contrast, the phosphorescence of $n\pi^*$ triplet ketones are blue shifted with solvent polarity, implying that the polar ground state is more effectively stabilized than the excited state. Benzophenone phosphorescence undergoes a -1.0 kcal/mol shift, switching from EPA to MCH. The $\Delta\mu_{ex}$ of benzophenone triplet is known from Stark effect measurements to be -1.7 D in the neat crystal.[67] The sulfoxides clearly show the same trend, with lower triplet energies in methylcyclohexane than in EPA, but the shifts are substantially larger. A simple-minded comparison based on the Lippert equation[61] would suggest that the sulfoxides have $\Delta\mu_{ex}$values of -2.2 to -2.9 D for those in the -3 to -5 kcal/mol range; **6-SO** may have a $\Delta\mu_{ex}$ as large as -4 D. It is possible, too, that the very large observed shift is due to specific solvent-solute interactions (*e.g.* hydrogen bond) that become nonstabilizing or destabilizing in the excited state because of charge transfer against the S-O dipole.

However, the crude estimates that we draw from the spectral shifts are less important for their exact magnitude than for their implication that the triplets are less polar than the ground state. The permanent dipoles of dimethyl sulfoxide and several of the current compounds are shown in Table 7. The relative independence of the dipole comes from charge separation along the S-O bond. *Ab initio* calculations on DMSO confirm that the vast majority of the total dipole comes from the S-O charge separation.[68] While we cannot accurately estimate the actual triplet dipoles, it is abundantly clear that the charge density on oxygen is substantially lower in the triplet than in the ground state.

Table 7. Dipole moments of sulfoxides in the ground state.[69-71]

Compounds	dipole moment (D)
1-SO	4.0
3-SO	4.2
5-SO	4.0
6-SO	3.9
7-SO	4.4
8-SO	4.5
12-SO	2.6
DMSO	4.0

2.4 Summary

The luminescent properties of a series of aromatic sulfoxides at 77 K have been characterized, along with several of the corresponding sulfides and sulfones. The following observations and conclusions can be made.

First, the phosphorescence of aromatic sulfoxides is generally very weak. Most of the observed quantum yields are under 0.05 and many are <0.01. The phosphorescence yields of the corresponding sulfides are much higher and the triplet energies are generally lower.

Second, the triplet energies of aromatic sulfoxides are fairly high, a few kilocalories per mole higher than the corresponding ketones. Diaryl sulfoxides appear to have triplet energies about 3 kcal/mol lower than the corresponding aryl methyl sulfoxides.

Third, the triplet states are delocalized onto the aromatic ring and involve charge transfer away from the sulfoxide oxygen. This is shown by large (3-10 kcal/mol) blue shifts in the phosphorescence on switching from nonpolar (methylcyclohexane) to polar (EPA) solvent.

Fourth, it is not clear at this stage whether the low phosphorescence yields of the sulfoxides are due to low intersystem crossing yields, relatively efficient nonradiative decay from the triplet to the ground state, or both.

2.5 Experimental Section

General instrumentation.

All luminescence spectra and lifetimes were recorded with an Edinburgh Instruments FL900 spectrometer. A suprasil liquid nitrogen immersion dewar was used to hold samples at 77 K. The samples were contained in 5-mm suprasil cylindrical tubes within the dewar. Compounds were checked for purity using a Hewlett-Packard 5890 II gas chromatograph (GC) equipped with HP-1 or DB-17 capillary columns and a flame ionization detector. UV / visible absorption measurements were performed with a Shimadzu PC-3101 spectrophotometer. NMR spectra were obtained using either a Nicolet or Varian 300 MHz instrument.

Compounds.

Commercially available materials were purified by flash chromatography on silica, distillation, sublimation, or recrystallization until no impurities were detected by GC (>99.9%). All of the rest of the compounds are known, and satisfactory spectroscopic data were obtained for each.

Phenoxathiin (6-S) was prepared by the method of Suter.[72]

***p*-Fluorophenyl methyl sulfoxide (2-SO),**[73,74] **phenoxathiin S-oxide, (6-SO),**[75] **and dibenzothiophene S-oxide (7-SO)**[75] were obtained by oxidation of the corresponding sulfides[72] with $Bu_4N^+IO_4^-$ and catalytic (5,10,15,20-tetraphenylporphine)iron (III) chloride.[75]

***p*-Methoxyphenyl methyl sulfoxide (3-SO)**[76] was prepared by oxidation of **3-S** by $NaIO_4$ in water.[77]

Dixylyl sulfoxide (9-SO),[78] **dimesityl sulfoxide (10-SO),**[78] **di-*p*-fluorophenyl sulfoxide (11-SO),**[79] **di-*p*-bromophenyl sulfoxide (13-SO),**[80] **and di-*p*-methoxyphenyl sulfoxide (14-SO)**[81] were prepared by condensation of the corresponding arene and thionyl chloride in the presence of $AlCl_3$.

***p*-Methoxyphenyl methyl sulfone (3-SO_2)**[82] **and phenoxathiin S,S-dioxide (6-SO_2)**[83] were prepared by oxidation of the corresponding sulfides with 30% aqueous hydrogen peroxide in refluxing acetic acid.[83]

General luminescence methods.

The solvent mixture for all luminescence experiments unless otherwise specified was a 5:5:2 mixture of either, isopentane, and ethanol (EPA). Isopentane and methylcyclohexane were spectro grade and were used as received. Absolute ethanol was refluxed over CaH_2 for at least 24 hours to remove carbonyl-containing compounds and the distilled freshly under Ar for each use. Ethyl ether was similarly handled. All samples were flushed with Ar for 10 minutes to remove oxygen. Luminescent lifetimes and spectra for triplet energies were obtained from samples that *ca.* 1 mM in chromophore. Control experiments showed that the lifetime measurements did not change on dilution of the samples. The spectrometer uses a xenon lamp which emits a pulse of a few new microseconds in duration, and the delay is collected using multichannel scaling. Due to an instrumentally imposed limitation, the lamp cannot be pulsed at a rate lower than 1 Hz. This leads to some uncertainty in lifetimes longer than about 0.5 s and can lead to some artifactual long components in decays. Data from very few samples with lifetimes under 200 ms could be satisfactorily fit to single exponential decays and were fit to distributions of exponentials using software provided by Edinburgh Instruments.

Phosphorescence quantum yields.

Quantum yield measurements were made using optically dilute samples. Solutions were prepared and the optical densities were measured using a standard 1-cm UV cell at room temperature. The concentration of the chromophore was adjusted such that the optical density (in the 1-cm cell) was ≤0.200 at the exciting wavelength, usually 265 nm. The samples were transferred to suprasil 5-mm cylindrical tube, and each was identically deoxygenated. A liquid nitrogen immersion dewar mounted in the spectrometer reproducibly positioned the samples. After the spectra were obtained and the spectral intensities were integrated, the data were corrected for variations in the measured optical density and compared to benzophenone ($\Phi_P = 0.74 \pm 0.02$).[39] Each reported value is the average of at least two measurements each on two independent samples, and the estimated error is ±20%.

Acknowledgment

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CHAPTER III

CHARACTERIZATION OF THE SINGLET AND THE TRIPLET AND PHOTORACEMIZATION OF METHANESULFINYL ARENES

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Woojae Lee and William S. Jenks

Abstract: The effect of a methanesulfinyl group on the photophysics of several aromatic chromophores has been investigated. Compared to the parent arenes, the spectroscopic singlet energies and the triplet energies are relatively unchanged by the substitution (±2 kcal/mol). The fluorescence quantum yields are reduced by at least one order of magnitude, whereas the phosphorescence quantum yields at 77 K are enhanced. Fluorescence lifetimes are greatly shortened, consistent with the reduced Φ_F. The triplet yields at room temperature are slightly enhanced by the substitution. Unusual fluorescence quantum yield enhancements are observed on cooling the samples to 77 K. For instance, a 15-fold increase of fluorescence of 1-methanesulfinylpyrene is observed upon freezing the sample whereas only a factor of 2 is seen in the unsubstituted pyrene. An attempt to relate the observed photophysics to

photoinduced racemization is made, since the photoracemization is negligible at 173 K. Racemization yields as a function of temperature have also been obtained. For methanesulfinyl pyrene, the activation barrier of photoracemization is estimated to be 2-7 kcal/mol.

3.1 Introduction

In the previous chapter (Chapter 2), an investigation into the triplet states of substituted phenyl and diphenyl sulfoxides was reported.[1] In most cases, fluorescence was not observed and very low phosphorescence was observed at 77 K. A bathochromic shift in phosphorescence of sulfoxide samples was observed when methylcyclohexane glass was used instead of polar EPA (5:5:2 mixture of ether:isopentane:ethanol) glass. The reason for low phosphorescence quantum yields was not clear - low intersystem crossing yields and relatively efficient non-radiative decay from the triplet to the ground state were both reasonable explanations. For this chapter, the research was focused on the effect of methanesulfinyl group as a substituent on the photophysics of several larger aromatic chromophores. The possible relation between the photophysics and the inversion of stereochemistry at sulfur center as a non-radiative decay pathway was also investigated.

The photophysical behavior of aromatic compounds is well known and reported.[2,3] Most unsubstituted aromatic hydrocarbons have fluorescence and persistent phosphorescence. The sum of fluorescence quantum yield and triplet yield for rigid aromatic hydrocarbons is usually close to unity.[4] The planar rigid structures (which constrain torsional-type oscillation) make them inefficient for radiationless deactivation of excited singlet state (S_1), and lead to an increase in fluorescence efficiency. Their moment of singlet-singlet transitions ($S_1 \rightarrow S_0$) is oriented in the molecular plane, whereas that of triplet-singlet transitions ($T_1 \rightarrow S_0$) is perpendicular to the molecular plane.[5,6] Usually vibronic structure is observed in their absorption and emission spectra due to the frequencies of fully-symmetric vibrations of the carbon skeleton.[2]

Substitution on aromatic rings leads to changes in the observed photophysics. Alkyl group substitution into the aromatic ring causes a modest red-shift of absorption and fluorescence spectra.[4,7] A greater effect was observed only when two alkyl groups were introduced into 1,4-positions of the same ring compared with the introduction of one alkyl group.[8] Phenyl and vinyl group substitution resulted in a significant red-shift and enhanced extinction coefficient, but this is clearly related to the extended conjugation. When a heavy atom (*e.g.*, bromine, iodine) is introduced, all intersystem crossing process rates are increased and it resulted in the decrease of quantum yield of fluorescence. In this case, spin-orbit coupling induces intersystem crossing. The effect of carbonyl group substitution onto the aromatic ring was observed with a similar pattern. By analogy, there is a possibility for sulfoxide group to show a heavy-atom effect or other spin-orbit coupling induced photophysical effects.

Sulfoxides with two different substituents are chiral. Their structure is known to be pyramidal at the sulfur atom. The relative ease of preparation of a single enantiomer of sulfoxides make them useful as a popular chiral auxiliary.[9,10] As part of our study on the photochemistry of sulfoxides, we have been interested in the photochemically induced stereomutation. Other mechanisms for inversion are well known.

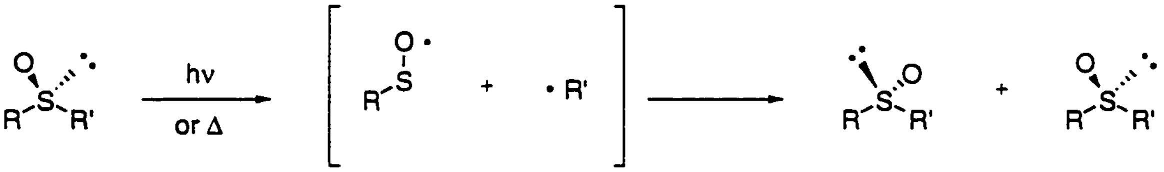


Figure 1a. Stereomutation by the α-cleavage mechanism.

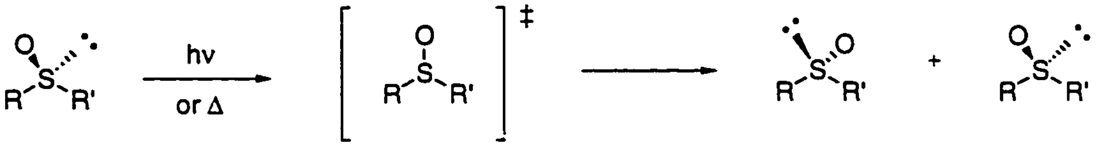


Figure 1b. Stereomutation by the pyramidal inversion mechanism.

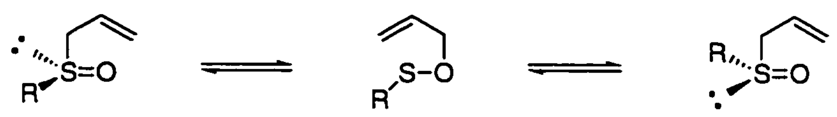
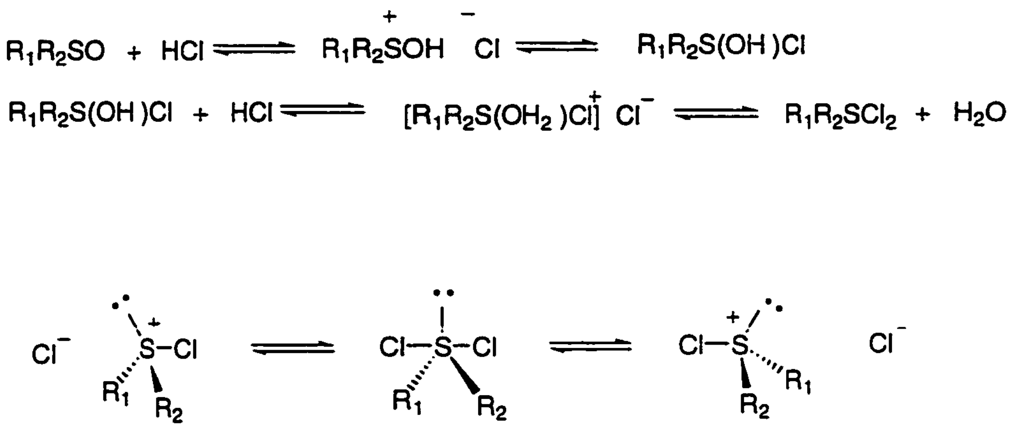


Figure 1c. Stereomutation by cyclic rearrangement.

The first thermal racemization of sulfoxide was reported by Krafft and Lyons in 1896.[11] The mechanistic study of this process was neglected until about 1960. The pioneering work on the mechanism of thermal racemization of sulfoxides was done by Mislow and his coworkers in late 1960s.[12-17] The three major mechanisms for the process are α-cleavage (Figure 1a), pyramidal inversion (Figure 1b), and cyclic rearrangement (Figure 1c). Cyclic rearrangement occurs only for allylic sulfoxides. The detail is reviewed in Chapter 1.

The stereomutation of sulfoxides has been induced by a variety of chemical reagents, such as acids (HCl, H_2SO_4, HI, HF, trifluoroacetic acid and phosphoric acid), acetic anhydride, nitrogen tetraoxide, and potassium *t*-butoxide.[16,18] Among them, the HCl reaction has been extensively investigated.[16,19,20] The prototypical stereomutation of sulfoxide by HCl is depicted in Figure 2. The structure of sulfodichloride was known to be a distorted trigonal bipyramid with chlorine atoms located at the apical positions.



$$R_1R_2SO + HCl \rightleftharpoons R_1R_2\overset{+}{S}OH\ \overset{-}{Cl} \rightleftharpoons R_1R_2S(OH)Cl$$

$$R_1R_2S(OH)Cl + HCl \rightleftharpoons [R_1R_2S(OH_2)Cl]^{+}\ Cl^{-} \rightleftharpoons R_1R_2SCl_2 + H_2O$$

Figure 2. Stereomutation by HCl.

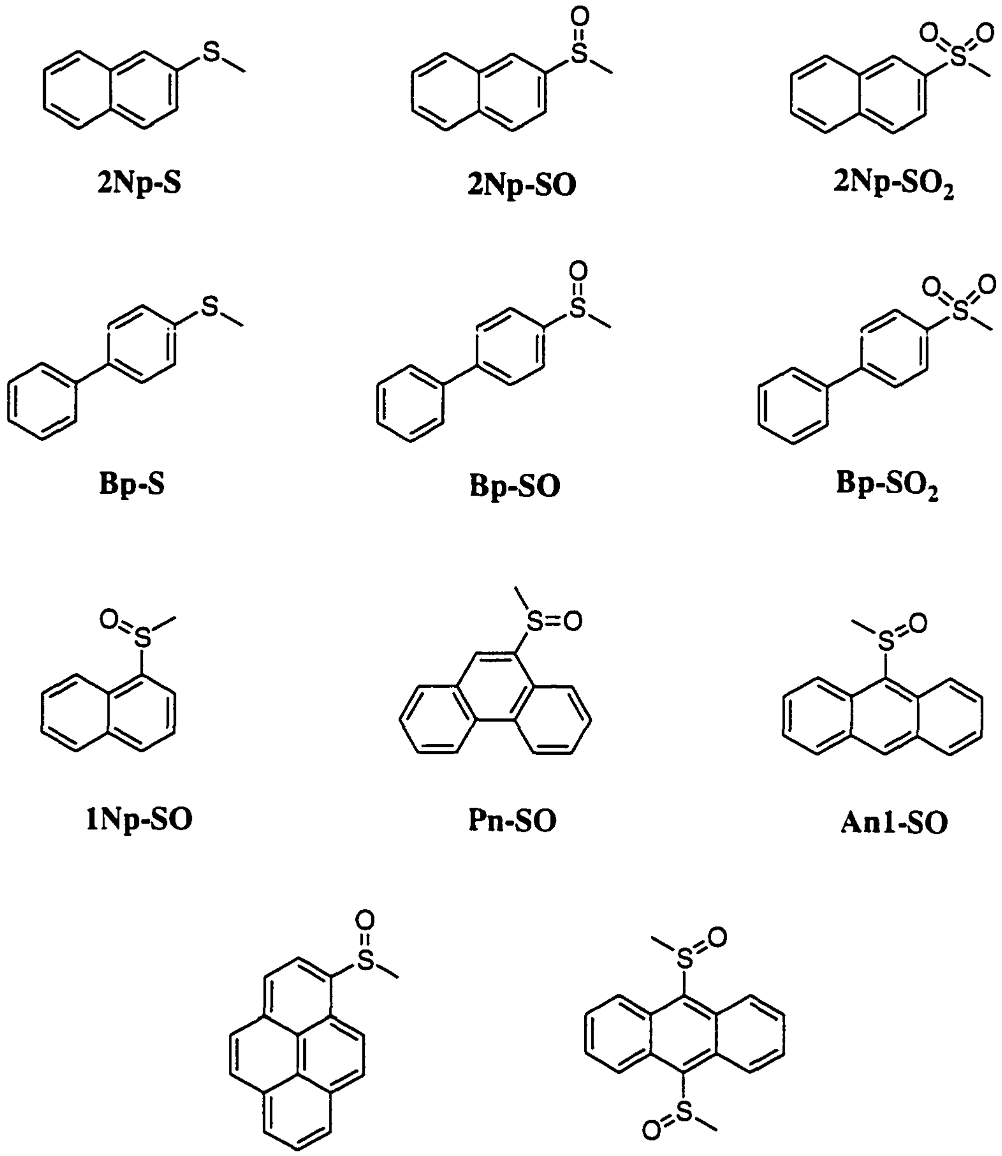
Mechanistic study for photochemical racemization also dates back to the mid 1960s by Mislow and Hammond.[16,21] At least two different explanations of this process were proposed; pyramidal inversion and α-cleavage due to a photochemical reaction.[16,22-25]

Hammond found that the use of naphthalene as a photosensitizer provided a higher yield of racemization than did direct irradiation. The mechanism of naphthalene sensitized stereomutation of *para* substituted phenyl methyl sulfoxides under photochemical reaction condition was studied by Cooke and Hammond.[26] Since both the singlet and the triplet energies of naphthalene were lower than the respective state energies of sulfoxides, exciplex formation between naphthalene and sulfoxide was suggested.[26,27] More recent work with a variety of substrates supports this mechanism and detail is described in Chapter 4.[28]

Recently, photoracemization of (*R*)-(+)-1-pyrenyl 4-tolyl sulfoxide was observed by Tsurutani and co-workers with the same efficiency in polymer matrices at room temperature as in solution.[29] In continuing effort, quantum yields of photoracemization in solution of chiral diaryl sulfoxides with various sizes of aromatic ring at room temperature were obtained.[30] The racemization yield was higher than the yield of decomposition from photolysis. Based on this result, simple configuration interaction singles (CIS) calculation and fluorescence measurements, they speculated that photoinversion occurred when electronic states change from n-σ^* excited states to the ground state.

Only a few examples of photoracemization of dialkyl sulfoxides without using photosensitizers have been reported in the literature.[31-34] This is because they do not observe convenient wavelengths of light and tend to undergo extensive decomposition on irradiation with high energy light.

Since there is no clearly proved mechanism beside α-cleavage with recombination of radicals and no systematic understanding of the electronic perturbation of an aromatic chromophore induced by sulfinyl substitution, the investigation of the mechanism of photoracemization of sulfoxide is very important. Our research in this dissertation focuses



2Np-S

2Np-SO

2Np-SO_2

Bp-S

Bp-SO

Bp-SO_2

1Np-SO

Pn-SO

An1-SO

Py-SO

An2-SO

Figure 3. Compounds used in the present study.

on establishing the relation between photophysics (such as fluorescence quantum yields, phosphorescence yields, singlet and triplet energies, lifetimes, chemical quenching, and so on) and stereomutation.

3.2 Results

3.2.1 Compounds

Methyl aryl sulfoxides, with differing arene moieties, were chosen to study. The compounds are illustrated in Figure 3. Also, optically resolved sulfoxides (**2Np-SO, Py-SO,** and **An1-SO**) were prepared, with optical resolution of 100%, within the HPLC detection error limit.

3.2.2 Emission spectra and spectroscopic excitation energies

The sulfoxides studied in Chapter 2 generally have benzene moieties. Weak phosphorescence was observed for all of these sulfoxides and fluorescence at 77 K was observed only three cases. No room temperature luminescence was obtained. Unlike these sulfoxides, the present methanesulfinyl aromatic compounds with bigger π-conjugated chromophores show photoluminescence both at room temperature and 77 K. At room temperature, fluorescence was observed from all of the sulfoxides, sulfides and sulfones in present study. HPLC grade acetonitrile was used as solvent.

At 77 K, various combinations of fluorescence and phosphorescence were observed: only fluorescence was observed from sulfoxides **An1-SO**, **Py-SO**, and **An2-SO**, only phosphorescence was observed from sulfoxide **Bp-SO** or both were observed from sulfoxides **2Np-SO**, **1Np-SO**, and **Pn-SO**. The detail is discussed in the following sections. All of the compounds were examined in 1:1 enthanol:methanol glass.

3.2.2.1 Singlet energies

The fluorescence spectra of most of the sulfoxides were very similar in appearance to those of the corresponding unsubstituted aromatic compounds. Their spectroscopic singlet energies were estimated and are listed in Table 1. The singlet energy was determined from the wavelength of intersection between the normalized emission and excitation spectra of the compounds (*e.g.*, Figure 4). The singlet energies of the sulfoxides are comparable to those of the corresponding unsubstituted aromatic compounds (within 4 kcal/mol), except **An2-SO**, which has two methanesulfinyl groups. There is no consistent dramatic effect observed, such as red-shift or blue-shift on the singlet energies by the substitution of methanesulfinyl group. The shapes of fluorescence spectra at 77 K were observed to be more structured than those at room temperature. No dramatic fluorescence shift was observed due to lowering the temperature.

Table 1. Spectroscopic singlet and triplet energies.

Compound	**E_S (kcal/ mol)[a]**	**E_T (kcal/ mol)[b]**
2Np-S	85	58
2Np-SO	91	61
2Np-SO_2	88	59
BP-S	90	61
BP-SO	98	69
BP-SO_2	96	64
1Np-SO	89	60
Pn-SO	85	69
An1-SO	73	*c*
Py-SO	78	*c*
An2-SO	65	*c*
Naphthalene[d]	92	61
Biphenyl[d]	94	66
Phenanthrene[d]	83	62
Anthracene[d]	76	43
Pyrene[d]	77	49

[a] These are obtained in acetonitrile at room temperature. [b] These are collected in 1:1 methanol and ethanol mixture at 77 K [c] No phosphorescence was observed. [d] These are reported in the literature.[4]

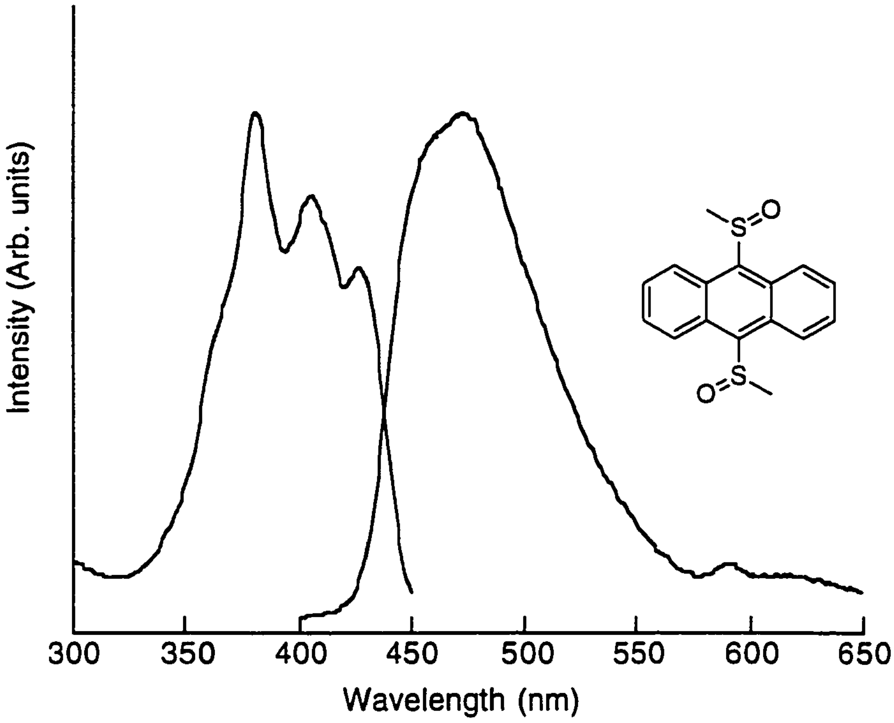


Figure 4. Excitation and emission spectra of **An2-SO** at room temperature in CH_3CN. E_s is taken to be 435 nm, the point of intersection. This figure is representative of the method used to obtain singlet energies.

For comparison, the singlet energies of a couple of representative sulfides and sulfones (naphthalene and biphenyl systems) were obtained and are also listed in Table 1. The singlet energies of sulfoxides and sulfones are greater than those of corresponding sulfides.

3.2.2.2 Triplet energies

The spectroscopic triplet energies of studied compounds were obtained from their phosphorescence spectra at 77 K using the method which is described in Chapter 2 (Table 1). Like the singlet energies, the triplet energies of sulfoxides are similar to those of the unsubstituted aromatic compounds (within 3 kcal/mol) except **Pn-SO** (7 kcal/mol). A slight blue-shift relative to the parent arenes was observed for all sulfoxides that have phosphorescence. The triplet energies of two different sulfides (**2Np-S** and **Bp-S**) and sulfones (**2Np-SO$_2$** and **BP-SO$_2$**) were obtained and are listed in Table 1. Like the singlet energies, the sulfoxides and sulfones have higher triplet energies than the corresponding sulfides. This trend was also observed in the previous study of phenyl sulfoxides (Chapter 2).

3.2.2.3 Solvent effects on triplet energies

The sulfoxides with significant phosphorescence in 1:1 methanol:ethanol glass were also examined in methylcyclohexane. Unlike the phenyl sulfoxide cases, no significant solvent effect was observed for the sulfoxides.

3.2.3 Quantum yields

The fluorescence quantum yields both at room temperature and at 77 K and the phosphorescence quantum yields of the sulfoxides, sulfides, and sulfones were obtained from integration of their spectra and are listed in Table 2. High fluorescence quantum yields and intersystem crossing yields but negligible phosphorescence quantum yields are common characteristics of unsubstituted aromatic compounds at room temperature.[2,4] Also, the sum of the fluorescence yields and triplet yields of most aromatic compounds is near unity. The parent aromatic compounds investigated this Chapter all have these characteristics.[4]

The sulfoxides examined here however, showed a completely different pattern of the photophysical behavior. The fluorescence quantum yields of the sulfoxides at room temperature range from 0.005 to 0.090, which is one or two orders of magnitude smaller than those of the corresponding unsubstituted aromatic compounds (Table 2).

The quantum yields of fluorescence of representative sulfides and sulfones at room temperature were also observed and are listed in Table 2. Their spectra were red-shifted

Table 2. Fluorescence and phosphorescence quantum yields.

Compound	Φ_F (R.T)	Φ_F (77 K)	Φ_{Ph} (77 K)
2Np-S	0.12	0.027	0.60
2Np-SO	0.015	0.044	0.22
2Np-SO$_2$	0.36	*a*	*b*
BP-S	0.18	0.08	0.59
BP-SO	0.005	0	0.53
BP-SO$_2$	0.26	0.04	0.41
1Np-SO	0.011	0.031	0.21
Pn-SO	0.013	0.066	0.41
An1-SO	0.09	0.19	~0
Py-SO	0.008	0.11	~0
An2-SO	0.010	0.33	~0
Naphthalene[c]	0.21	0.45	0.0039
Biphenyl[c]	0.15	0.14	0.24
Phenanthrene[c]	0.13	0.20	0.16
Anthracene[c]	0.27	0.34	0.0003
Pyrene[c]	0.72	0.92	0.0022

a Signal was too weak. *b* Data deviate too much for unknown reason. *c* These are reported in the literature.[4]

from those of the corresponding sulfoxides. Their fluorescence quantum yields are higher than those of the corresponding sulfoxides by more than an order of magnitude. This strongly suggests that the effect is not driven simply by the presence of the sulfur, but by the sulfinyl group in particular.

At 77 K, the fluorescence quantum yields of sulfoxides are enhanced by 3-13 times with the exception of the biphenyl system even though they are still much smaller than the unsubstituted aromatic compounds. The position of fluorescence is identical to the room temperature one, though the shape of spectra is more structured. This phenomenon is fairly unusual for simple aromatic compounds. The fluorescence quantum yields are not enhanced with lowered temperature for most aromatic compounds. If they are, the magnitude of the enhancement is generally small.

Strong phosphorescence was observed at 77 K for naphthalene, biphenyl, and phenanthrene systems. The phosphorescence yields for both **1Np-SO** and **2Np-SO** are 50 times greater than that for naphthalene. The phosphorescence enhancement due to methanesulfinyl group substitution by factor of 2 was observed for **Bp-SO** and **Pn-SO**. No phosphorescence was observed at 77 K for anthracene and pyrene systems. The fluorescence quantum yields at 77 K for the systems that did not phosphoresce were observed at least twice greater than the sulfoxides that phosphoresce.

Table 3. Quantum yields of triplet of sulfoxides.

Compound	**Φ_T (hexane)**	**Φ_T (CH_3CN)**
2Np-SO	0.12	0.18
BP-SO	0.12	0.12
1Np-SO	0.41	0.42
Pn-SO	0.22	0.24
Py-SO	0.50	0.35
An2-SO	0.07	0.07
Naphthalene[a]	0.75	0.80
Biphenyl[a]	0.84	*b*
Phenanthrene[a]	0.73	0.85
Anthracene[a]	0.71	0.66
Pyrene[a]	0.37	0.38

[a] These are reported in the literature.[4] [b] No report is in the literature.

The quantum yields of triplet formation were obtained indirectly by laser flash photolysis and detection of singlet oxygen O_2 ($^1\Delta_g$). They are listed in Table 3. The validity of singlet oxygen detection was examined by comparison to triplet-triplet energy transfer to β-carotene. The triplet yield of methanesulfinyl pyrene ($\Phi_T = 0.58$) in hexane was obtained by the laser flash photolysis in the presence of β-carotene. A very similar result ($\Phi_T = 0.50$) was obtained by using sinlget oxygen detection. All other triplet yields of sulfoxides were, therefore, obtained by using singlet oxygen detection. The measurements were done in two different solvents, polar (acetonitrile) and nonpolar (hexane) solvent, but there was no significant difference in the result. The triplet yields were lower than those of parent aromatic by a factor of two or more, except methanesulfinyl pyrene (higher in hexane and same in acetonitrile). Since both fluorescence yields and triplet yields of the sulfoxides decreased relative to the parent arenes, the sum of fluorescence yields and triplet yields is not clearly close to one.

All of these data strongly imply the existence of an efficient non-radiative decay process of the excited singlet state, which is dependent upon temperature. We propose that this is the photoracemization process of sulfoxides with a small barrier. This will be described more in detail in later at this chapter.

For comparison, the fluorescence and phosphorescence quantum yields of couple of sulfides (**2Np-S** and **Bp-S**) and sulfones (**2Np-SO$_2$** and **Bp-SO$_2$**) at both room temperature and 77 K were measured and also listed in Table 2. Their fluorescence yields at room temperature were much bigger than those of sulfoxides by at least one order of magnitude. For sulfones, the fluorescence yields at room temperature were even bigger than parent aromatic compounds. At 77 K, strong phosphorescence along with very weak fluorescence was observed for these sulfides and sulfones. There were difficulties to obtain the photoluminescence quantum yields at 77 K for **2Np-SO$_2$**. The fluorescence was too weak to identify for **2Np-SO$_2$**, and the baseline of phosphorescence was too irregular to obtain consistent data. This has been a problem even though the sample was repeatedly purified by recrystallization and sublimation.

3.2.4 Lifetimes

The fluorescence lifetimes obtained by time-correlated single photon counting both at room temperature and at 77 K and are listed in Table 4. Along with the decrease of their fluorescence quantum yields, the fluorescence lifetimes of sulfoxides were shorter than those of unsubstituted aromatic compounds. The lifetimes at 77 K were same or slightly increased from those at room temperature, which is typical as for aromatic compounds. The longer

Table 4. Lifetimes at room temperature and at 77 K.

Compound	**τ_F (R.T), ns**	**τ_F (77 K), ns**	**τ_{Ph} (77 K), s**
2Np-S	13	*a*	>1[b]
2Np-SO	*12*[c]	*13*	*>1*[b]
2Np-SO_2	11	*a*	>1[b]
BP-S	1.9	*a*	>1[b]
BP-SO	*4*	*a*	*0.79*
BP-SO_2	2.7	*a*	>1[b]
1Np-SO	11	10	>1[b]
Pn-SO	2	37	>1[b]
An1-SO	1	*a*	*d*
Py-SO	1.3	82	*d*
An2-SO	*a*	10	*d*
Naphthalene[e]	105	273	2.6
Biphenyl[e]	16	*f*	4.6
Phenanthrene[e]	61	63	3.6
Anthracene[e]	5.8	605	0.04
Pyrene[e]	190	515	0.58

[a] Signal was too weak to measure the lifetime. [b] The lifetime is longer than the upper limit with our instrument. [c] This might come from sulfide, not sulfoxide. [d] No phosphorescence was observed. [e] These are reported in the literature.[4] [f] No report is in the literaure.

fluorescence lifetimes were expected for sulfoxides at low temperature since the non-radiative decay processes were limited with temperature lowering.

The lifetimes of sulfides and sulfones were observed and are listed in Table 4. Even though their fluorescence quantum yields are greater than those of the corresponding sulfoxides, their lifetimes were comparable to those of sulfoxides. Based on previous work experience, the existence of even very small quantities of highly emissive impurities such as sulfides and sulfones in the sulfoxides, even though the amount of them is too small to detect by GC or HPLC, can lead to artifactual lifetime data. In order to minimize this artifact, all of the sulfoxides for this study were purified repeatedly by recrystallization and sublimation. Despite this, with the combination of lifetime data and fluorescence quantum yield data, the presence of highly emissive material in the **2Np-SO** and **Bp-SO** is strongly suspected.

All of the sulfoxides except **Bp-SO** have longer phosphorescence lifetimes than 1 second, which is the upper limit that can be determined with our instrument. Such exteneded lifetimes are typical of aromatic hydrocarbons. They indicate that there is not an extra efficient non-radiative decay pathway out of the triplet states.

3.2.5 Racemization

Sulfoxides with two different substituents are chiral. The quantum yield of inversion was defined as either the formation of the new enantiomer per photon, or the loss of original chiral compound per photon during the photoreaction in the absence of other significant photochemistry.

Photolysis of chiral sulfoxides was done with a Xe-Arc lamp and monochromator set at 295 nm. The concentration of samples was about 0.3 mM in both acetonitrile and methylcyclohexane. For 0 to 40 °C measurements, a regular rectangular quartz cell was used for photolysis. For -100 °C measurements, a specially designed sample holder with ESR tube to actually contain the sample was used (see experimental section for details). Both argon degassed and air-saturated samples were tested and they gave the identical amounts of enantiomers under the same photolysis conditions. No other significant photolysis products except enantiomers of sulfoxides were observed by chiral HPLC until the racemization was completed. In order to minimize secondary photoreactions, such as back-inversion from product enantiomer to starting material, all of the quantitative photoracemization data were collected with less than 10% loss of starting materials. The quantum yields of inversion at various temperature were obtained and are listed in Table 5. Three sulfoxides were chosen to study because they had clear separation in a HPLC chiral column. All of the data in Table 5 were averages of at least 3 indepent measurements and the error was about 10%.

The quantum yield was calculated by the following equation:

Table 5. The quantum yields of inversion at different temperatures.[a, b]

Compounds	Φ_{inv}				
2Np-SO	0.27 (39 °C)	0.25 (25 °C)	0.22 (10 °C)	0.20 (0 °C)	0.0030 (-100 °C)
An1-SO	0.25 (41 °C)	0.22 (22 °C)	0.21 (10 °C)	0.18 (0 °C)	0.0021 (-100 °C)
Py-SO	0.20 (39 °C)	0.18 (25 °C)	0.15 (10 °C)	0.13 (0 °C)	0.0020 (-100 °C)

[a] At least three measurements were done for all entries.

[b] The errors are within 10% of averages for each compound.

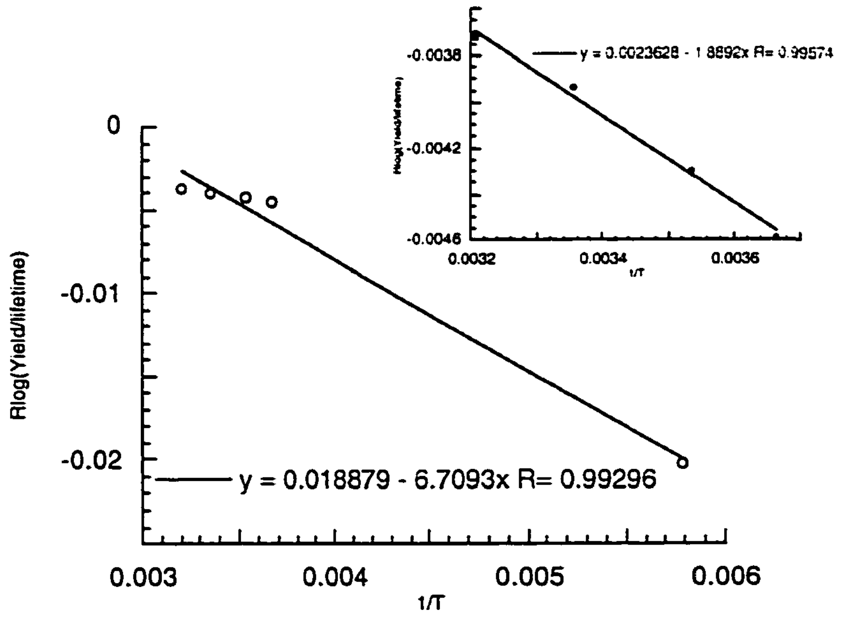


Figure 5. Arrhenius plot for activation barrier.

$$\Phi_{inv} = \frac{CV}{I_0 t} \qquad \text{(Eq 1)}$$

In this equation, quantum yield is proportional to the product of concentration of the product (C) and volume of the solution (V). The reciprocal of the product of the intensity of the light (I_0) and the irradiation time (t) is also proportional to the quantum yield. The intensity of light was obtained using azoxybenzene actinometry.[35]

For methanesulfinyl pyrene case, the activation barrier for racemization at excited state was estimated to be about 7 kcal/mol, which is much smaller than the ground state racemization barrier (Figure 5). The fluorescence lifetimes of methanesulfinyl pyrene remain the same at near room temperatures (0 to 40 °C) The lifetime at -100 °C was estimated to be 50 ns based on the assumption that the lifetime gets longer linearly with lowered temperature. The activation barrier was obtained from the slope of the Arrhenius plot. Only 2 kcal/mol activation barrier was obtained from the first 4 near room temperature data points (inset graph in Figure 5).

To figure out which state is responsible for the photoracemization, the photolysis of 2-methanesulfinyl naphthalene with triplet sensitization by benzophenone and triplet quenching by isoprene and piperylene were done. Irradiation from 350 nm bulbs was used for the sensitization experiments. The sulfoxide used do not absorb at this wavelength. No racemization was observed when benzophenone was introduced to 2-methanesulfinyl naphthalene solution in a period of time of irradiation that the sulfoxide under direct irradiation was completely racemized. No inhibition of racemization was observed when isoprene and piperylene were introduced in 0.3 mM 2-methanesulfinyl naphthalene solution respectively as a triplet quencher up to 25 mM. Also the presence of oxygen did not interfere the efficiency of photoracemization and disappearance of 2-methanesulfinyl naphthalene. These combined results provided the evidence that the photoracemization occurred via excited singlet states.

3.3 Discussion

One of the distinctive features of photophysics of various methanesulfinyl arenes is the loss of fluorescence. Not only at room temperature, but also at 77 K, the fluorescence of all sulfoxides are very weak. A similar result was observed for several aryl *p*-tolyl sulfoxide by Tsurutani and his coworkers.[30] No fluorescence was observed for sulfoxides with small aromatic rings and conjugation such as phenyl *p*-tolyl sulfoxide and naphthyl *p*-tolyl sulfoxide, but very weak fluorescence was observed for sulfoxides with large aromatic rings and high conjugation such as phenanthrenyl *p*-tolyl sulfoxide and pyrenyl *p*-tolyl sulfoxide. All of the observation was made at the room temperature.

For ketones and aldehydes, the greater fluorescence yields were obtained when the size of aromatic ring is bigger.[30,36] This trend was not observed in this study. Unlike ketone photochemistry, in which the intersystem crossing is very efficient, sulfoxide has efficient non-radiative process from the singlet excited state such as racemization. Therefore, it is not necessary to show the same trend.

Even though the phosphorescence yields of sulfoxides are enhanced from the parent arenes, it is not reasonable to call this a heavy atom effect, because the room temperature triplet yields of sulfoxides were not enhanced. Rather, this behavior supports the presence of efficient non-radiative decay from the singlet excited states.

Photoracemization at room temperature is observed being very efficient. With temperature lowering, it is negligible. The fluorescence enhancement at 77 K can be explained by this. Also, the longer fluorescence lifetime at 77 K supports the inhibition of non-radiative decay at 77 K.

3.4 Summary

Both chiral and racemic methanesulfinyl arenes with various ring sizes were prepared and the basic photophysical parameters were obtained such as quantum yields of luminescence, lifetimes and so on. The sulfinyl group has effects on the photophysics to enhance the phosphorescence yields but lower fluorescence yields for the aromatic chromophores. Symmetry lowering and effective non-radiative process (racemization) are possible explanations for the observation.

Racemization occurs from the singlet excited states. Both the loss of fluorescence and relatively small changes in triplet yields with methanesulfinyl substitution and the results of the use of triplet quenchers and the sensitizer support this conclusion. Also, the racemization seems to occur via pyramidal inversion process with small activation barrier, even though we report no direct evidence for this process. Since no decomposition products were observed under the photolysis conditions, α-cleavage is not an efficient process. Therefore, it is unlikely that photoracemization occurs via α-cleavage/recombination mechanism.

3.5 Experimental Section

General instrumentation

All luminescence spectra and lifetimes were recorded with an Edinburgh Instruments FL900 spectrometer and a Spex FluoroMax fluorometer. For fluorescence, specially designed screw-capped fluorescence cuvettes were used for the best sealing efficiency. A transparent suprasil liquid nitrogen immersion dewar was used to hold samples at 77 K. At this temperature, the samples were contained in 5-mm suprasil cylindrical tubes within the dewar. At room temperature, square 1 cm path length cells were used. Compounds were checked for purity using either a Hewlett-Packard 5890 II gas chromatograph (GC) equipped with HP-1 or DB-17 capillary columns and a flame ionization detector or a Hewlett-Packard 1050 series HPLC equipped with a Hypersil ODS column and a diode array detector. The chiral column for HPLC is CHIRACEL OB model made by Daicel Chemical Industries, LTD. The eluent was the hexane and isopropanol mixture (80:20) for all analyses. For a representative case, the retention times for 2-methanesulfinylnaphthalene enantiomers were 10 and 14 minutes. UV / visible absorption measurements were performed with a Shimadzu PC-3101 spectrophotometer. NMR spectra were obtained using a Varian 300 MHz instrument.

All of the fluorescence measurements at room temperature were done in acetonitrile and all the 77 K measurements were done in either 1:1 methanol and ethanol mixture as a polar solvent or methyl cyclohexane as a nonpolar solvent. HPLC grade acetonitrile and methanol were used and they were dried using sodium sulfate for each use. Ethanol was held at reflux over calcium hydride until required and then distilled under dry argon for each use.

Compounds

In this study, two types of sulfoxides were prepared. One group is the racemic mixture and the other is as a single enantiomer. All of the sulfoxides in the same type were prepared using same synthetic method, so that two specific syntheses will be described by one example for each type. All of the sulfoxides used in the study were purified by column chromatography, recrystallization and sublimation as needed. For recrystallization, an ethanol and water (95:5) mixture was used.

No characterization to determine the stereochemistry at the sulfur atom of all enantiomerically pure sulfoxides was done since it is not important for this study. However, since 2-methanesulfinylnaphthalene was obtained from the Grignard reaction of (*S*R)-sulfinate, which was synthesized and characterized by Guo in our lab, it is assumed to be (*S*S)-sulfoxide. This enantiomer came out earlier in HPLC analysis. The rest of sulfoxides also came out earlier than their enantiomers in HPLC; they too are assumed to be (*S*)-sulfoxides.

Synthesis of 9-(methanesulfinyl)anthracene (racemic mixture). Under argon gas, 1.82 mmol of 9-bromoanthracene was dissolved in 20 ml anhydrous ether. The solution was chilled down to -20 °C. Into the solution, 2.2 equivalents *t*-BuLi were added, followed by stirring for 30 minutes at -20 °C. At this point, 3 mmol of methyl disulfide was added to the reaction mixture, and it was stirred for another 30 minutes at the same temperature. The reaction temperature was allowed to warm to room temperature and the mixture was stirred overnight. It was then washed with aqueous NH_4Cl to remove unreacted organolithiums, and then extracted with ether. The product 9-(methylthio)anthracene was produced in over 70% yield and purified by column chromatography.

The oxidation from sulfide to sulfoxide was done by hydrogen peroxide (1 equivalent) in acetone at room temperature for 10 hours and the product 9-(methanesulfinyl) anthracene was extracted by ether. It was purified by column chromatography. The product yield after purification was 50%. Column chromatography using silica with hexane and methylene chloride (25:75 mixture) provides good separation of sulfoxides from sulfides and sulfones. After the recrystallization using the ethanol and water mixture (95:5), 100% purity of sulfoxides was obtained, as determined by HPLC analysis. All of sulfoxides and sulfides were prepared with the same manner. Their product yields were nearly the same as that of 9-methanesulfinylanthracene. Since **An2-SO** has two methanesulfinyl groups, it was prepared as mixture of diastereomers. This made the interpretation of NMR peaks in the aromatic regions difficult. Also, the singlet peak for the methyl groups is not really singlet but two singlets with very small difference on their chemical shifts. The preparation was in the literature but new NMR data of **Py-SO**[37] and **An2-SO**[38,39] are reported below. The NMR data and other characterization of the rest of the sulfoxides and the sulfides are matched the ones in the literature.[40-49]

^{1}H NMR of **Py-SO**[37] ($CDCl_3$, 300 MHz) δ 2.92 (s, 3 H, CH_3), 8.07-8.31 (m, 7 H, aromatic), 8.40 (d, 1 H, J = 8.2, aromatic), 8.68 (d, 1 H, J = 8.2, aromatic).

^{1}H NMR of **An2-SO**[38,39] ($CDCl_3$, 300 MHz) δ 3.01 (2 overlapping singlets, 6 H, 2 CH_3), 7.62-7.83 (m, 6 H, aromatic), 8.33 (dd, 1 H, $J = 3.3$, $J = 5.7$, aromatic), 9.06 (dd, 1 H, $J = 3.3$, $J = 6.9$, aromatic). The area ratio of peak at 8.33 and 9.06 is 1.4:1.0.

Synthesis of optically resolved 1-methanesulfinyl pyrene.[50] Sodium 1-pyrenesulfonate (1.52 g, 5 mmol) from Aldrich was suspended in DMF. While being stirred, 3 ml (1.1 equivalents) of thionyl chloride was added over a period of about 5 minutes. After stirring for an additional 45 minutes, the reaction mixture was poured into 40 ml of ice water. The precipitate was filtered and washed with water. The precipitate was 1-pyrenesulfonyl chloride and it was dried. It was purified by recrystallization from methylene chloride and hexane. The yield of this step was 75%. The NMR spectra matched those in the literature.[51]

Pyrenesulfonyl chloride 0.67g (2.1 mmol) and *l*-menthol 0.22g (1.4 mmol) were dissolved in 20 ml methylene chloride in a three-neck round-bottom flask under argon gas which was equipped with a reflux condenser. Triethylamine (0.3 ml, 2.1 mmol) and trimethyl phosphite (0.33 ml, 2.8 mmol) were introduced by syringe through a rubber septum from the side arm. After the rubber septa were replaced by the glass stoppers, the reaction mixture was refluxed for 24 hours. After it was cooled to room temperature, it was poured into a mixture of ether (20 ml) and 1 M HCl (7 ml). The ether layer was treated with saturated sodium bicarbonate and brine. Then it was dried by sodium sulfate. The product was purified by column chromatography using silica and recrystallization. The product was diastereomerically pure menthyl-1-pyrenesulfinate[52] and the yield was 30%.

Menthyl 1-pyrenesulfinate (156 mg, 0.39 mmol) was dissolved in 30 ml dried ether. The solution was chilled to -78°C in a dry ice/acetone bath. To this solution, 0.5 ml (1.5 mmol) of 3M methylmagnesium bromide was added. The usual acidic workup was done after 24 hour reaction. The ee was checked by use of a chiral column in the HPLC against racemic material and was >99%. The NMR, IR and UV spectra matched with racemic 1-methanesulfinylpyrene. The NMR of all three chiral sulfoxides are matched the ones in the literature by using either same or different synthetic routes.[53-55] Also, the single HPLC peak came out at exactly same retention time as one of enantiomers in racemic mixtures. The product yield was 30%.

Two other resolved sulfoxides were prepared, 2-methanesulfinylnaphthalene and 9-methanesulfinylanthracene. The same experimental procedure was taken for the synthesis from sulfonic chloride to chiral sulfoxide for these two compounds. The product yields of these two sulfoxides were also about 30%. Resolved naphthalene sulfoxide were prepared from (*S*R)-menthyl-2-naphthalenesulfinate.

Synthesis of tetrabutylammonium 9-anthracenesulfonate.[56] Chlorosulfonic acid (6.7 ml) was added to ice-cold dioxane (100 ml). While the temperature of the solution was maintained at less than 10 °C, 13.82 g of anthracene was added over 5 minutes while being stirred by magnetic stirrer. The reaction mixture was heated to 40 °C for 30 minutes. It was cooled to room temperature and then it was poured into the ice water (150 ml). The precipitate was removed by filtering with celite. NaOH was added to the solution until the pH was 9. To the solution, tetrabutylammonium hydroxide (40 wt%, 48.9 ml) was added. By the extraction with methylene chloride, followed by recrystallization from EtOAc/Et_2O, tetrabutylammonium anthracenesulfonate was obtained in 72% yield. The NMR was identical to the one in the literature.[56]

Synthesis of 9-anthracene sulfonic chloride.[57] Tetrabutylammonium 9-anthracenesulfonate 27.82 g (0.056 mol) was dissolved in acetonitrile (30 ml). Sulfolane (28 ml) and $POCl_3$ (20.5 ml) were added to the solution. The reaction mixture was heated to 68 ~ 72 °C for 40 minutes. It was cooled to 5 °C and then 140 ml of ice-cold water was added dropwise. It was stirred for another 10 minutes. The product was filtered and then dissolved in methylene chloride. Sodium sulfate was added and then 9-anthracenesulfonyl chloride was obtained by removing methylene chloride with 60% yield. The NMR spectrum was identical with the literature.[57]

Actinometry

Azoxybenzene was used for an actinometer.[35] Its quantum yield was known as 0.017 over 250 nm - 450 nm range. Azoxybenzene (10 mg) was dissolved in 10 ml of ethanol

(95%) and water (5%). In a cuvette, 3.6 ml of the solution was taken and 254 nm light was incident from Xe-Arc lamp. After 5 minutes of irradiation, it was diluted with 2 ml, 4 ml, and 9 ml of 1M KOH ethanol(95%)/water(5%) solution. KOH solution was filtered before used. UV absorbance of 2-hydroxyazobenzene was obtained after dilution at 458 nm. The extinction coefficient of azoxybenzene at 458 nm is 7600. By Beer's law, the concentration was determined. Only 1.4% conversion was obtained for 5 minute irradiation at 254 nm.

The 1 mM (*S*)-2-methylsulfinylnaphthalene samples were completely racemized within 5 minutes at 254 nm using a rayonet photoreactor that is a more efficient light source. Weaker radiation was needed for the low conversion experiments, so the Xe-Arc lamp was used.

The same technique was used for the low temperature setup. The actinometry was done at room temperature using an EPR tube in the L-shaped sample holder for low temperature photolysis.

Quantum yield of racemization measurement at different temperature

Photolysis of chiral sulfoxides was done with Xe-Arc lamp at 295 nm. The concentration of samples was about 0.3 mM in both acetonitrile and methyl cyclohexane. The optical densities of the samples were over 1.0 at 295 nm. A brass sample holder that allowed for internal fluid circulation and held standard 1 cm cells was used. The sample holder was connected to a temperature regulated circulator (RMT 6, LAUDA) from

Brinkmann, which controlled the sample temperature. The actual sample temperature (0 - 40 °C) was measured repeatedly while the cell was inside in the holder for 30 minutes. Ordinary quartz cells closed with septa used for the photolysis in this temperature range.

For 173K photolysis, a temperature controller (ER4111VT made by Bruker), which was originally designed for ESR temperature control, was used. It operates by boiling liquid nitrogen and heating it under the control of a thermostat. A transparent optical dewar was configured for photolysis while cold N_2 was passed over the sample. An EPR tube was used as the sample holder for the photolysis. An L-shaped sample holder, made from quartz, was designed to hold the EPR tube while cold nitrogen gas passed through it. The error range of temperature was less than 10 °C for this low temparature setup. The temperature uncertainty for the room temperature setup was about 1 °C. At the various temperatures, the sample was photolyzed 2-10 minutes. The disappearance of the starting chiral compound and appearance of the enantiomer was checked by HPLC chiral column. The maximum conversion was less than 10% and no other photoproducts were observed.

Quenching and sensitizing experiment

Benzophenone was used as a triplet sensitizer to figure out which excited states of chiral sulfoxide leads to photoracemization. Benzophenone was used after being recrystallized. Irradiation from 350 nm bulb in the rayonet photoreactor was used for the sensitization experiments. At this range of irradiation, nearly all the light is absorbed by 5 mM benzophenone under these conditions, but there is a small residual absorption by 3 mM 2-methanesulfinylnaphthalene when the sensitizer is absent. Two samples were irradiated at the same time, one containing the sensitizer and one not. No racemization was observed in the presence of benzophenone while the latter racemized completely.

To quench the excited triplet state, isoprene and piperylene were used as quenchers over a concentration range of 0.3 - 25 mM. The sample was 2-methanesulfinylnaphthaleme in CH_3CN. Photolysis was done with Xe-Arc lamp at 295 nm. At this wavelength, the OD of sulfoxide samples was over 1.0. No light was absorbed by quenchers. The same extent of racemization was observed both with and without quenchers. Also, the air-filled (20% oxygen) sample showed same amount of racemization as the argon-degassed sample under indentical photolysis conditions.

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CHAPTER IV

MECHANISMS OF EXCITED STATE QUENCHING BY AROMATIC SULFOXIDES

Based on a paper published in the *Journal of Physical Chemistry*[1]

Paul Charlesworth, Woojae Lee, and William S. Jenks

Abstract: 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 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.

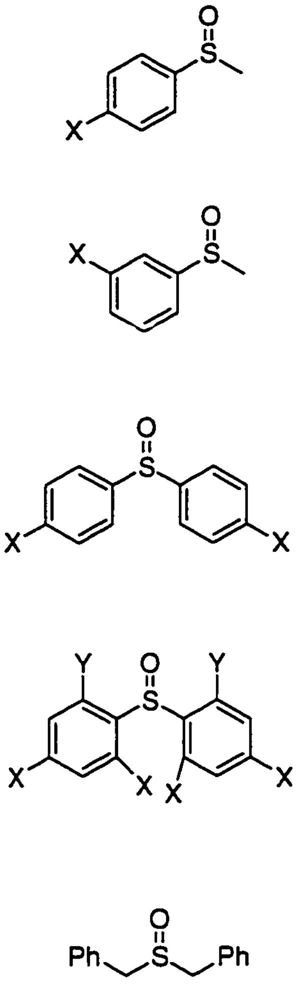
4.1 Introduction

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 sulfoxide is underdeveloped.[4] Recently, systematic study have been made on the various aspects of photochemistry of sulfoxides and were reviewed by Jenks group.[5] 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.[6-8] 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.[9] 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).[10]

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.[11-14] 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.[13,14] 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."[14] 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.

An extensive set of measurements has been conducted 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 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.



1, X = H   X = F
X = CH_3 X = Br
X = CH_3O X = CF_3

2 X = CF_3

3, X = H   X = Br
X = F   X = CH_3
X = Cl   X = CH_3O

4 X = CH_3; Y = H
5 X = Y = CH_3

6

Chart 1. Sulfoxides used in the present study.

4.2 Results

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**-CH_3, and **1**-Br in acetonitrile). The rate constants for Np were measured in

Table 1. Singlet quenching rate constants and redox potentials for various sulfoxides.

	k_q (10^7 $M^{-1}s^{-1}$)[a]						
	naphthalene		1-aminonaphthalene	pyrene	2,3-dimethylnaphthalene	$E_{pk/2}$[b] (V)	
sulfoxide	C_6H_6	CH_3CN	CH_3CN	CH_3CN	CH_3CN	reducn	oxidn
1-H	3.4 ± 0.1	4.5 ± 0.1			1.8 ± .1	-2.47	1.9
1-CH3	3.47 ± 0.04	4.5 ± 0.1			1.5 ± .1	-2.35	1.82
1-CH3O	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-CF3	246 ± 8	202 ± 2	1160 ± 30		545 ± 20	-2.11	2.00
2-CF3	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

Table 1. continued.

	k_q (10^7 $M^{-1}s^{-1}$)[a]						
	naphthalene		1-aminonaphthalene	pyrene	2,3-dimethylnaphthalene	$E_{pk/2}$[b] (V)	
sulfoxide	C_6H_6	CH_3CN	CH_3CN	CH_3CN	CH_3CN	reducn	oxidn
3-Br	590 ± 29	368 ± 17	1270 ± 20		810 ± 50	-1.88	2.05
3-CH3	46.7 ± 1.8	47.2 ± 1.1	483 ± 14		19 ± 1	-2.39	1.88
3-CH3O	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.

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.[15,16] 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. 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 shown in Table 2 and Figure 1.

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 obtained against the oxidative values (Figure 2). 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

Table 2. Electrochemical peak and half-peak potentials.

Sulfoxide	E_{red} (V)[a]	E_{red} (Peak,V)[a]	E_{ox} (V)[a]	E_{ox} (Peak,V)[a]
1-H	-2.58	-2.65	2.10	2.20
1-CH_3	-2.50	-2.62	2.00	2.10
1-CH_3O	-2.83	-2.91	1.86	1.93
1-F	-2.64	-2.73	1.97	2.20
1-Br	-2.20	-2.30	2.05	2.24
1-CF_3	-2.25	-2.34	1.98	2.15
2-CF_3	-2.40	-2.48	2.10	2.20
3-H	-2.29	-2.34	2.11	2.34
3-F	-2.19	-2.22	2.22	2.22
3-Cl	-2.10	-2.18	2.24	2.24
3-Br	-1.97	-2.04	2.24	2.24
3-CH_3	-2.43	-2.47	2.00	2.10
3-CH_3O	-2.50	-2.58	-	-
4	-2.40	-2.45	1.96	2.03
5	-2.39	-2.44	1.73	1.80
6	-2.76	-2.80	2.30	2.40

[a] Values are relative to SCE. See text for further details.

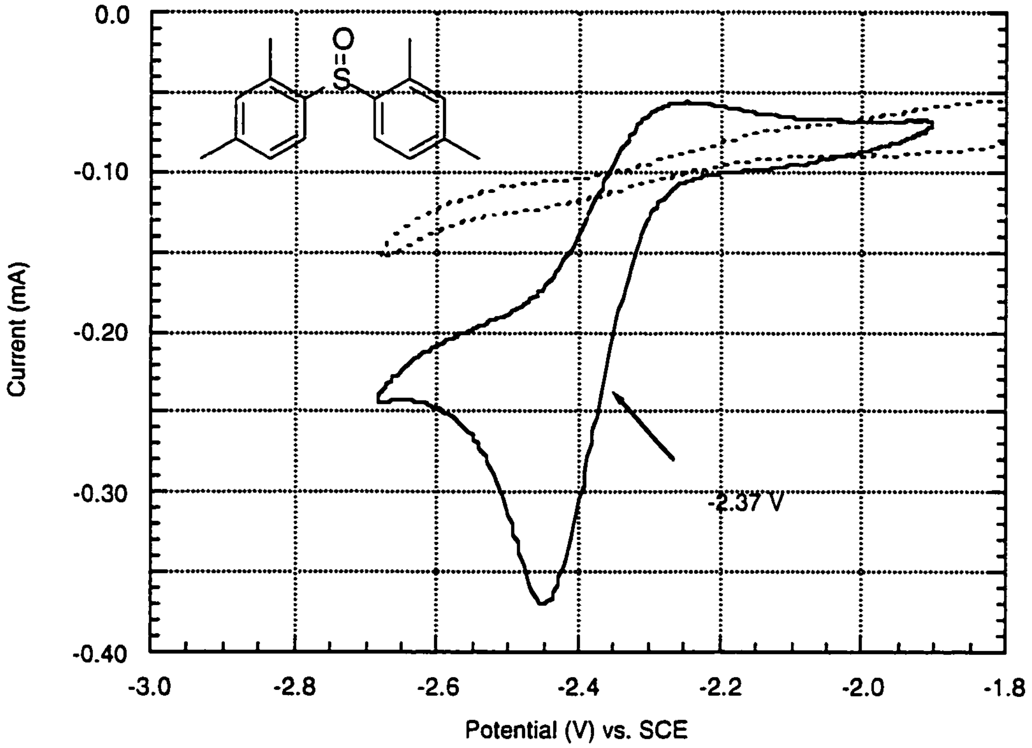


Figure 1. Cyclic voltammetry plot for compound **4**. After compensating for background, $E_{pk/2}$ is at -2.37 V.

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

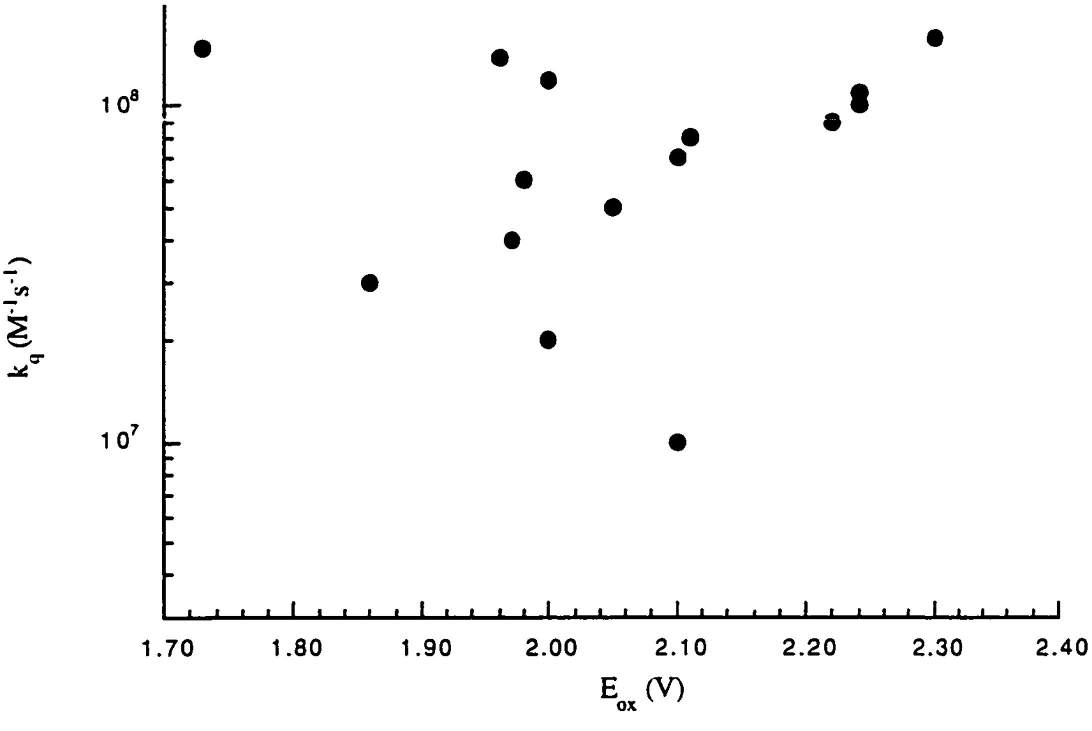


Figure 2. Rate constants for quenching of singlet naphthalene plotted against the oxidation potential of sulfoxides.

surrogate. The correlation of the rate constants with this value is shown in Figure 3. (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

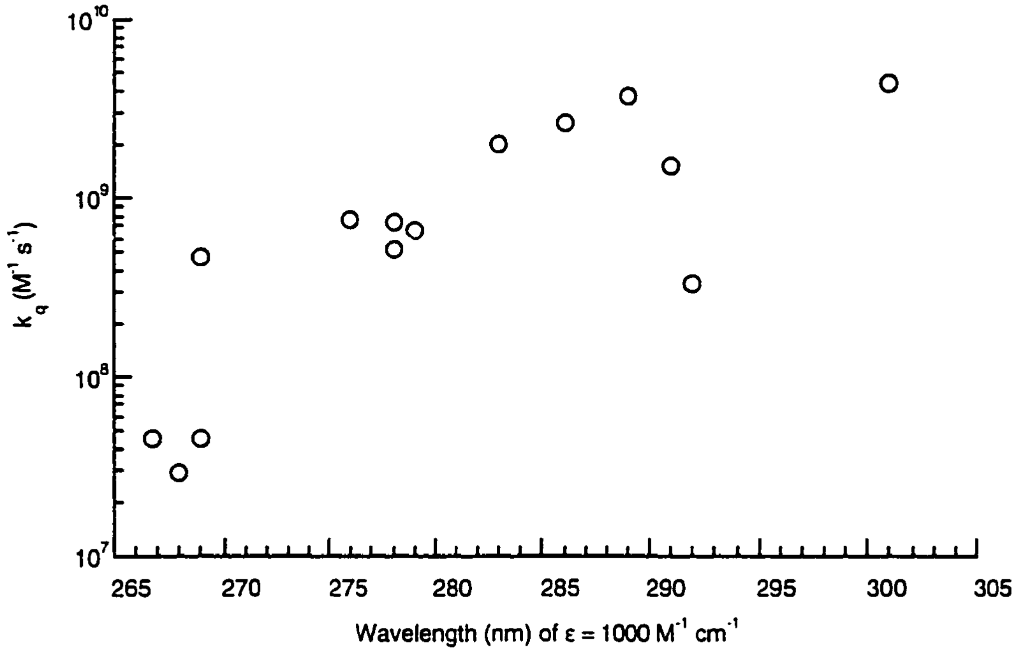


Figure 3. Rate constants for the quenching of singlet naphthalene plotted against the wavelength at which the sulfoxide molar absorption coefficient reaches 1000 $M^{-1}cm^{-1}$.

constants and λ_{max} of any absorption band. Though there is a significant correlation in Figure 3, 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 photophysical parameters for the sensitizers are presented in Table 3.

4.3 Discussion

The energetics of photoinduced electron transfer in the "normal" region can be approximated for a related series of compounds by [18]

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

Table 3. Photophysical parameters of the sensitizers.[17]

sensitizer	Spectroscopic singlet energy[a] (eV)	Potential (V) oxidation[b]	Potential (V) reduction[c]
naphthalene	3.99	1.54	-2.49
1-aminonaphthalene	3.37	0.54	
2,3-dimethylnaphthalene	3.87	1.38	-2.64
pyrene	3.33	1.16	-2.09

[a] in polar solvent. [b] in acetonitrile, *vs*. SCE. [c] in DMF, *vs*. SCE.

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.[19-21] In acetonitrile, C is typically ignored because of the 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 above, is shown in Figure 3. No similar correlation is observed for oxidation of the sulfoxides and reduction of the sensitizers.

As plotted in Figure 4, 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 4 is a fit of all of the acetonitrile rate constant data to the Rehm-Weller equation 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 $E_{pk/2}$ values are available.

Like the previous work,[14] 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

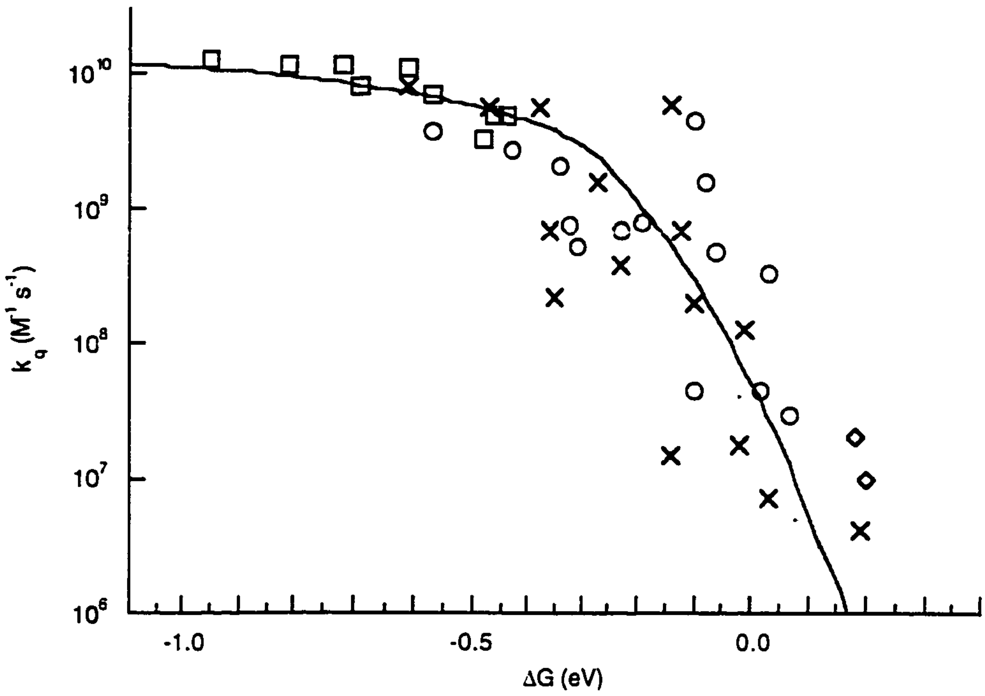


Figure 4. Rate constants for quenching of various sensitizers by the sulfoxides plotted against ΔG for electron transfer (see text). The squares correspond to 1-aminonaphthalene, the circles are naphthalene, the crosses are 2,3-dimethylnaphthalene, and the diamonds are pyrene.

and Hammond[13,14] 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.

4.4 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 sulfoxides, but further conclusions based only on Np quenching are difficult 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.

4.5 Experimental section

General. Commercially available sensitizers and sulfoxides were repetitively recrystallized from ethanol until GC traces indicated a purity of ≥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 VXR 300 MHz instrument.

Methyl *p*-(trifluoromethyl)-phenyl sulfide. To a solution of *p*-bromo-(trifluoromethyl)-benzene (2.86 g, 12.7 mmol) in ether (25 ml), chilled to -25 °C, was slowly added *tert*-butyllithium (in hexane, 28.3 mmol). After 30 minutes, dimethyl disulfide (1.5 ml, 16.7 mmol) was added in one portion. After 30 more minutes, the solution was warmed to room temperature and allowed to stir overnight. After ordinary aqueous workup, chromatography (hexane on silica) afforded the sulfide (1.79 g, 9.3 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J =8.4 Hz, 2 H), 7.51ppm (d, J = 8.4 Hz, 2 H), 2.51ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 126.3 (q, J_{CF} = 33 Hz), 125.6 (q, J_{CF} = 3 Hz), 125.6, 124.3 (q, J_{CF} = 270 Hz), 15.0.

Methyl *p*-(trifluoromethyl)-phenyl sulfoxide (1-CF_3). To a solution of methyl *p*-(trifluoromethyl)-phenyl sulfide (0.96 g, 4.3 mmol) in chloroform (20 ml) was added tetrabutylammonium periodate (2.11 g, 4.9 mmol) and 50 mg 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride. After stirring at room temperature for a week, the reaction mixture was evaporated onto 2-3 g of silica and deposited on the top of an ordinary silica column. The sulfoxide (570 mg, 2.4 mmol, 56%) was isolated as white crystals by elution with dichloromethane and subsequent sublimation. ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 4 H), 2.66 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150, 133 (q, J = 37.5 Hz), 126.5, 124.5 (q, J_{CF} = 275 Hz), 124.0, 43.5.

Methyl *m*-(trifluoromethyl)-phenyl sulfide. This compound was prepared in analogous fashion to the para isomer in 82% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 - 7.5 (m, 4 H), 2.51 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.2, 131.3(q, J_{CF} = 32 Hz), 129.4, 129.1, 124.0 (q, J_{CF} = 271 Hz), 122.7 (q, J_{CF} = 4 Hz), 121.6 (q, J_{CF} = 4 Hz), 15.5.

Methyl *m*-(trifluoromethyl)-phenyl sulfoxide (2-CF_3). This compound was prepared in analogous fashion to the para isomer in 52% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1 H), 7.81 (d, J = 9 Hz, 1 H), 7.75 (d, J = 9 Hz, 1 H), 7.66 (t, J = 9 Hz, 1 H), 2.74 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 132.0 (q, J_{CF} = 33 Hz), 130.0, 127.8 (q, J_{CF} = 4 Hz), 126.9, 123.5 (q, J_{CF} = 271 Hz), 120.6, 43.5.

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 minutes 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 mm^2) 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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CHAPTER V

GENERAL CONCLUSIONS

The luminescent properties of a series of aromatic sulfoxides at 77 K have been characterized, along with several of the corresponding sulfides and sulfones.

The project was begun with a series of benzene-based aromatic sulfoxides. Their phosphorescence was generally very weak. Most of the observed quantum yields are under 0.05 and many are <0.01. The phosphorescence yields of the corresponding sulfides are much higher and the triplet energies are generally lower.

The triplet energies of these aromatic sulfoxides are fairly high, a few kilocalories per mole higher than the corresponding ketones. Diaryl sulfoxides appear to have triplet energies about 3 kcal/mol lower than the corresponding aryl methyl sulfoxides.

Even though triplet characterization from weak phosphorescence provides some basis to understand the photochemistry of sulfoxides, it is not ideal for relating the photophysics to photochemistry of sulfoxides due to the lack of singlet characterization. Therefore, the study of sulfoxides that were more likely to have both singlet and triplet photoluminescence and do not decompose well was needed. Methanesulfinylarenes with bigger ring sizes are the proper compunds for this study. Both optically resolved and racemic methanesulfinylarenes with various ring sizes were prepared and the basic photophysical parameters were obtained such as quantum yields of luminescence, lifetimes and so on.

For this set of larger arenes, the sulfinyl substituent enhances the phosphorescence yields at low temperature but lowers the fluorescence yields. Symmetry lowering and effective non-radiative process are possible explanations for the observation. The temperature dependence of racemization, lifetimes, and quantum yields imply that racemization is the non-radiative decay pathway.

Racemization occurs from the singlet excited states. Both the loss of fluorescence and relatively small changes in triplet yields with methanesulfinyl substitution and the results of the use of triplet quenchers and the sensitizer support this conclusion. Also, the racemization seems likely to occur via pyramidal inversion process with a small activation barrier, even though we report no direct evidence for this process. Since no decomposition products were observed under the photolysis conditions, α-cleavage is not a likely explanation.

Aromatic sulfoxides are found to quench aromatic sensitizers whose singlet and triplet energies are significantly lower than their own. This is relevant to various reports of sensitized photochemistry including stereomutation reactions. 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 sulfoxides, but further conclusions based only on Np quenching are difficult 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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