

Photodeoxygenation of Dibenzothiophene Sulfoxide: Evidence for a Unimolecular S–O Cleavage Mechanism¹

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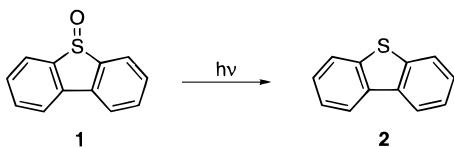
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Abstract: Photolysis of dibenzothiophene sulfoxide results in the formation of dibenzothiophene and oxidized solvent. Though quantum yields are low, chemical yields of the sulfide are quite high. Yields of the oxidized solvents can also be high. Typical products are phenol from benzene, cyclohexanol, and cyclohexene from cyclohexane and 2-cyclohexenol and epoxy cyclohexane from cyclohexene. A number of experiments designed to elucidate the mechanism of the hydroxylation were carried out, including measurements of quantum yields as a function of concentration, solvent, quenchers, and excitation wavelength. These data are inconsistent with a mechanism involving a sulfoxide dimer, which also does not properly account for the solvent oxidations. It is suggested that the active oxidizing agent may be atomic oxygen O(³P) or a closely related noncovalent complex, based on the nature of the oxidation chemistry, comparison to known rate constants for O(³P) reactivity, and the quantum yield data.

Introduction

The oxidation of benzene to phenol during the course of the nearly quantitative photochemical deoxygenation of dibenzothiophene sulfoxide (**1**) to dibenzothiophene (**2**) was a result that immediately grabbed our attention. We recently communicated this and other hydrocarbon functionalizations.² With this paper, we report a series of experiments designed to determine the mechanism of the deoxygenation and a further investigation of the oxidation reactions.



Posner³ and Shelton⁴ independently and nearly simultaneously published their observations of the photochemical deoxygenation of a number of aromatic sulfoxides. Since then, other examples in which deoxygenation is the principal photochemistry have been observed,^{5–7} and the sulfide is reported as a minor or trace product in a number of other instances.^{6–14} In the vast majority

of cases, as for **1**, the lack of observation of sulfone rules out a disproportionation mechanism.^{15,16}

Two different mechanisms have been proposed in the literature to account for this reaction. The first of these was explicitly suggested by Shelton⁴ and implied by Posner.³ Laid out in Figure 1, we shall refer to it as “the dimer mechanism.” The precise structure of the dimer **4** is less important than the notion that an excited triplet sulfoxide **3** is trapped by another ground state molecule **3**, leading to an intermediate that ultimately produces two sulfides **5** and molecular oxygen, O₂.

An alternative mechanism was later proposed on the basis of a series of chemically induced dynamic nuclear polarization (CIDNP) measurements.^{10,11} We shall refer to it as “the sulfinyl mechanism,” illustrated in Figure 2. Its first step is an α -cleavage reaction to produce the sulfinyl radical **7**, which is well preceded in sulfoxide photochemistry. The critical transformation, though, is the reduction of the sulfinyl radical to the sulfenyl radical **9** by means of oxygen transfer to another species. While not specified completely, this is assumed to be another radical in solution. Recombination of the sulfenyl and alkyl radicals generates the sulfide.

Both the sulfinyl mechanism and the dimer mechanism (providing ¹O₂ is produced) would be expected to induce oxidation of solvent substrates. Indeed, Posner’s suggestion of ¹O₂ production (path A, Figure 1) was based on isolation of an oxidized substrate (*vide infra*). In a preliminary report, we showed that photolysis of **1** results in oxidation of the solvent.² However, the scope of the oxidation is sufficiently broad that singlet oxygen is an unlikely candidate. In this paper, we report additional oxidations and further investigation into the mechanism of photodeoxygenation of dibenzothiophene sulfoxide. We conclude that, at least for **1**, neither the sulfinyl nor the dimer mechanism is correct. We speculate that the oxidizing agent may be a ground-state oxygen atom O(³P) produced by a unimolecular dissociation of the SO bond.

Despite its fundamental importance, we are unaware of any previously reported method for cleanly producing O(³P) in

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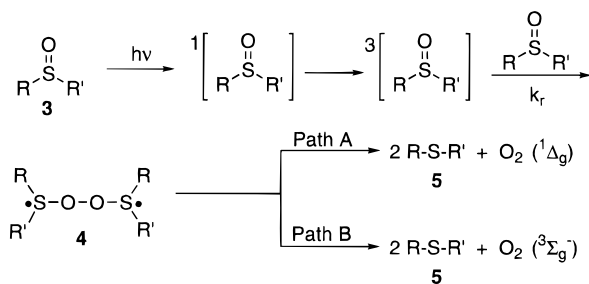


Figure 1. "Dimer mechanism". In path A, the dimer collapses to yield the sulfides and singlet oxygen. In path B, molecular oxygen is produced in its ground state.

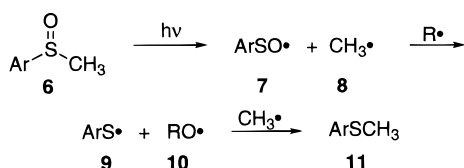


Figure 2. "Sulfinyl mechanism".

solution, in contrast to the workable methods available for gas-phase study. We make a strong circumstantial case that photolysis of dibenzothiophene sulfoxide may be just such a convenient solution-phase method. Photolysis of **1** requires only modestly energetic light ($\leq \sim 350$ nm), does not have any important competing reactions, and does not inherently bring other oxidizing species (*e.g.*, O₂) into solution.

Experimental Section

Materials. Dibenzothiophene sulfoxide **1** was prepared by oxidation of **2** with Bu₄N⁺IO₄⁻, catalyzed by (5,10,15,20-tetraphenylporphine)-iron(III) chloride.¹⁷ All solvents except *cis*- β -methylstyrene were commercially available. When necessary as indicated by GC traces, they were purified by distillation, typically from LiAlH₄ or CaH₂. Cyclopentadiene was freshly cracked before use. GC analysis was used to check for oxygenated impurities in solvents immediately before their use. EPA is an acronym for a 5:5:2 mixture of ethyl ether, 2-methylbutane, and ethanol.

Gas Chromatography. Gas chromatographic (GC) analyses were carried out on a Hewlett-Packard 5890 instrument equipped with a flame ionization detector. Most analyses were carried out using a Hewlett-Packard HP-1 capillary column of 10 m. The remainder (typically those involving separation of alcohol isomers) were carried out using a 25 m HP-20 column or a 30 m DB1701 column. GC-MS analysis was carried out with a Finnigan benchtop Magnum instrument, which uses ion trap detection and a DB-5 column for separations.

Luminescence. Phosphorescence spectra were measured using an Edinburgh FL-900 spectrometer. Spectra obtained at 77 K were obtained using a quartz 5 mm NMR tube and a quartz liquid nitrogen immersion Dewar flask, as previously described.¹⁸

Irradiations: General. Two systems were used for irradiation. The first was a Southern New England Ultraviolet Rayonet mini-reactor that had been modified to have both a fan and magnetic stirring. The 300 nm bulbs were used, which emit a wide band centered at approximately 300 nm. The fan keeps the solution temperature at ambient levels. The second system was a Photon Technologies, Inc., 150 W Xe lamp focused directly on a monochromator used to select the wavelengths of irradiation. Typically, it was used with slit widths allowing ± 12 nm linear dispersion from the quoted wavelength. Samples are put in a permanently mounted cell in such a way that all the exiting light hits the sample cell without further focusing. Photolysis of valerophenone to yield acetophenone was used as an actinometer.¹⁹ For variable-wavelength studies, azoxybenzene was used as the

actinometer.²⁰ Quantum yield data using the two actinometers varied by no more than 10%. For quantum yield measurements in which the initial absorption was less than 2, corrections were made to compensate for the incomplete absorption of light. For all quantum yield measurements, photolyses were stopped at low conversion (<20%), and sulfide yield was nearly quantitative. Oxygen was removed from all samples either by flushing with argon or by freeze-pump-thaw (FPT) degassing.

Oxidation Experiments: General. Unless otherwise reported, the following conditions were observed for all the oxidation experiments. Samples were degassed by the FPT method. Conversions of **1** were moderately low, typically $\leq 25\%$. Starting concentrations were 1–5 mM. The lowest concentrations were for alkane solvents, where solubility of **1** was a limitation. In a few instances, as noted, cosolvents were used. Most typically, dichloromethane was the solvent of choice. Essentially identical oxidation results were obtained for cyclohexane and cyclohexene with and without a cosolvent. Product identifications were done by comparison to authentic samples with GC and GC-MS. Individual response factors were determined for all compounds.

Product Identifications and Quantification. All product identifications were made by comparison with authentic samples, either obtained commercially or prepared by standard literature methods. GC-MS was the major method of comparison. Cyclohexene was assayed as the dibromide, formed by bubbling of Br₂ through photolyzed solutions until color was persistent, followed by Ar flushing to remove the excess Br₂ before injection. Because Br₂ is known to oxidize sulfides, quantification of formation of **2** was handled in separate injections. Hexadecane was used as an internal standard, and molar response factors were determined for all products relative to it.

Octene Oxidations. The *cis*- and *trans*-4-octenes were individually purified by distillation from LiAlH₄. Freshly distilled alkenes were used to prepare the solutions, which contained 10 mM **1**, 10% alkene by volume, and either acetonitrile or dichloromethane. No significant difference in results was observed between the two solvents. Photolyses were carried out using Rayonet 300 nm bulbs in quartz glassware. The resulting allylic alcohols were not separated from one another, but all other products were. Control experiments showed that neither the alkenes nor the epoxides isomerized under the reaction conditions. Oxidation of the alkenes with *m*-CPBA provided an assessment of their purity. Less than 1% *cis*-epoxide was obtained from *m*-CPBA oxidation of the *trans*-olefin, and about 5% *trans*-epoxide was obtained from *m*-CPBA oxidation of the *cis*-octene.

***cis*- and *trans*- β -Methylstyrene.** *trans*- β -Methylstyrene was purified by two successive distillations from LiAlH₄. Palladium-catalyzed hydrogenation of 1-phenylpropyne followed by purification with a silica column (hexane) afforded 99.1% pure *cis*- β -methylstyrene.

Freshly distilled *trans*- β -methylstyrene was used to prepare the solutions, which contained 6 mM **1**, 10% alkene by volume, and benzene or CH₂Cl₂ as solvent. Photolysis of the *trans*-alkene solution was carried out at 320 ± 12 nm, using the Xe arc lamp. The *cis*- and *trans*-alkenes along with both epoxides and cinnamyl alcohol were characterized by GC. Analysis after photolysis showed no isomerization of the alkene had occurred within experimental error. A control experiment showed that the neither of the epoxides isomerized during the photolysis conditions.

A mixture of 10% *cis*- β -methylstyrene (by volume) and 10 mM of **1** in benzene was photolyzed at 340 ± 12 nm with the 150 W Xe arc lamp. Control experiments showed that 15–17% of the alkene isomerized during the photolysis. However, no epoxide isomerization occurred under the photolysis conditions.

Isotope Effect Experiments. Benzene and benzene-*d*₆ were used as received. Mixtures of approximately 1:3, 1:1, and 3:1 of the respective isotopomer pairs were used to determine selectivities. Quantification of the two phenols was done by analysis of the molecular ions using the ion trap GC-MS equipped with a 30 m DB-5 column. Response factors against an internal standard for the two phenols were not identical, but were accounted for. The benzene and benzene-*d*₆ solutions and 10 mM **1** were photolyzed in the Rayonet mini-reactor (20–22% conversion of **1**). Similar methods were used for cyclohex-

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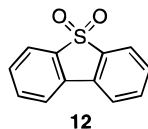
ane, save for differing solvent ratios. Cyclohexene, as usual, was assayed as the dibromide.

Singlet Oxygen Trapping. Singlet oxidation was generated by visible irradiation of oxygen-containing solutions with methylene blue as a sensitizer. Verification of singlet oxygen production was obtained by quantitative oxidation of dibenzyl sulfide (11 mM) to dibenzyl sulfoxide at 0 °C, which took less than 2 h. In the absence of methylene blue or light, no oxidation of dibenzyl sulfide took place. A solution of 1 mL of 1-methylcyclohexene, 4 mL of CDCl₃, and methylene blue was photolyzed at 0 °C for 4 h with air bubbling. NMR analysis of the solution immediately after photolysis showed the appearance of two broad singlets at 7.4 and 7.9 ppm, attributed to hydroperoxides. These peaks disappeared on addition of D₂O or on standing at room temperature for 1 h. In the latter case, a new peak at 4.8 ppm appeared, which also disappeared on addition of D₂O. Also, the just-photolyzed solution could be added in equal portion to a test reagent solution of 21 mM dibenzyl sulfide. Analysis of the mixture after standing at room temperature for a few minutes provided dibenzyl sulfoxide. When the photolyzed solution was allowed to stand for 1 h before mixing with the dibenzyl sulfide test reagent, no sulfoxide was obtained. Identical experiments, carried out with cyclohexene, rather than 1-methylcyclohexene, produced no exchangeable NMR peaks or sulfide oxidation.

Results

The photoreduction of **1** was found to be a well-behaved, one-photon process. The absorption spectrum of **1** extends out to about 350 nm; from this and the fluorescence spectrum, the spectroscopic singlet energy is taken as 82 kcal/mol.^{18,21} On the basis of phosphorescence data at 77 K, the spectroscopic triplet energy is 61 kcal/mol in polar solvent and 58 kcal/mol in nonpolar solvent.¹⁸ When the deoxygenation reaction is carried out to modest conversions ($\leq 25\%$), the yield of sulfide **2** is essentially quantitative in all solvents. The yield of sulfide after complete conversion of sulfoxide ranges from 70 to 100% in different solvents, with quantitative conversion being observed in benzene, in agreement with Posner.³ While oxygen was not found to affect the quantum yield for loss significantly, it did affect some product distributions.

Photochemical disproportionation of **1** to the sulfide **2** and the sulfone **12** was ruled out by product study. Under no circumstances was the sulfone observed. In principle, **12** could have been formed and then undergone subsequent photochemistry, perhaps much more efficiently than **1**, such that it was not observed. In a separately published study,²² it was shown that **12** is virtually photoinert in many solvents, benzene in particular. However, it is reduced to biphenyl on photolysis in 2-propanol. Biphenyl was not observed.



The quantum yield of formation of **2** from **1** was measured under a variety of conditions. One important issue was the influence, if any, of the initial concentration of **1** on the quantum yield. As shown in Figure 3, no significant concentration effect is observed over a range of about 0.5–30 mM.

In Table 1 are given the quantum yields as a function of solvent. In each case, the value is the average of at least three independent measurements, and the error limits are standard deviations. The initial concentration of **1** in alkane solvents is limited by solubility. The quantum yield was also measured

(21) The value of 85 kcal/mol in ref 18 is a typographical error. The correct value is 82 kcal/mol.

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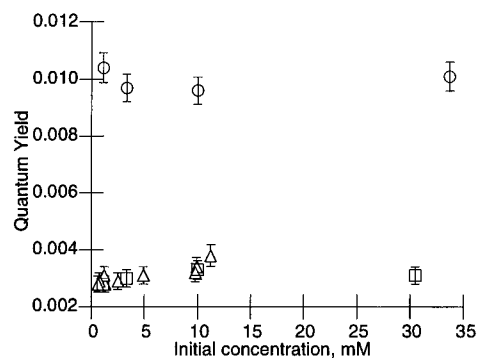


Figure 3. Quantum yield for formation of dibenzothiophene (**2**) as a function of initial concentration of **1**. Circles: THF solvent, 270 nm excitation. Squares: THF solvent, 320 nm solvent. Triangles: benzene, 320 nm excitation.

Table 1. Quantum Yield of Formation of Dibenzothiophene with 320 ± 12 nm Irradiation

solvent	quantum yield	[1] ₀
acetonitrile ^a	0.0026 ± 0.0004	0.50
benzene ^a	0.0030 ± 0.0003	1.30
cyclohexane	0.0030 ± 0.0002	0.50
cyclohexene	0.0100 ± 0.0004	1.32
cyclohexene ^b	0.0080 ± 0.0002	1.20
2,2-dimethylbutane	0.0029 ± 0.0003	0.30
dimethyl sulfoxide	0.0079 ± 0.0005	2.15
Freon 113 (CCl ₂ FCF ₂ Cl) ^a	0.0024 ± 0.0003	0.22
hexane ^a	0.0029 ± 0.0004	0.33
2-methylbutane	0.0031 ± 0.0003	0.28
2-propanol ^a	0.0034 ± 0.0003	1.67
tetrahydrofuran	0.0028 ± 0.0003	1.11
tetrahydrothiophene	0.0085 ± 0.0002	3.10
toluene ^a	0.0028 ± 0.0003	1.89

^a Oxygen removed by Ar flushing, rather than FPT degassing. ^b 10% AcOH added.

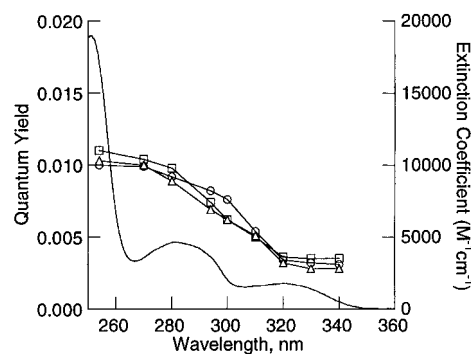


Figure 4. Quantum yield as a function of excitation wavelength and absorption spectrum in THF. Initial concentrations for quantum yields: 0.24 mM in hexane (circles), 1.5 mM in acetonitrile (squares), 3.0 mM in THF (triangles). The line without illustrated points is the absorption spectrum.

as a function of excitation wavelength. Samples of fixed concentrations were irradiated at different wavelengths, and azoxybenzene was used as the actinometer. The data are shown in Figure 4. The UV spectrum is obtained with < 2 nm resolution, whereas the quantum yields were measured with light with 24 nm total linear dispersion. Thus, we interpret the data to imply that the increase in quantum yield coincides with the onset of the second significant absorption band. There does not appear to be another increase in quantum yield on going to the third major UV band.

A significant issue in mechanistic organic photochemistry is the identity of the excited state(s) from which reaction occurs, and diene quenching experiments are one of the classical

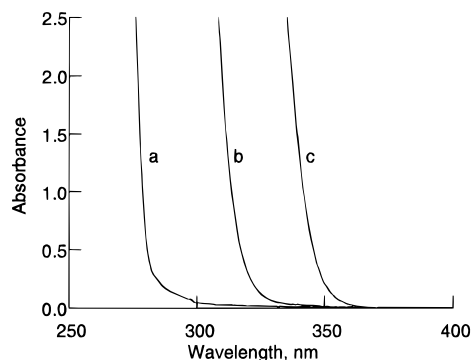


Figure 5. Absorption spectra of (a) neat benzene, (b) 100 mM Ph₂SO in benzene, and (c) 2.10 mM **1** in benzene.

methods of testing for long-lived triplet states.²³ As a first attempt, isoprene was used as a potential triplet quencher and quantum yields were measured as a function of its concentration. Rather than a drop in quantum yield, an increase of 15–40% was observed when 1.23 M (10%) isoprene was added to acetonitrile, benzene, Freon 113, hexane, 2-propanol, or toluene. No decrease was noted in any solvent. It was recognized that the triplet energy of isoprene is about 60 kcal/mol,²⁴ high enough that there might be some ambiguity in the interpretation of these data. However, neither cyclopentadiene (triplet energy 58 kcal/mol;²⁴ concentrations up to 1 M) nor O₂ (1 atm saturated, ca. 9 mM) quenched the reaction in benzene.

Several experiments were run that were attempts to test the dimer mechanism explicitly. The first of these was to photolyze a mixture of sulfoxides (**1** and another compound) in which **1** could be selectively irradiated. With an excess of the other sulfoxide available, asymmetric dimers **4** would be formed, and both sulfides would be observed on analysis. Diphenyl sulfoxide undergoes photochemical deoxygenation, though not quantitatively.³ It was felt that Ph₂SO would be an acceptable “quencher” sulfoxide for **1**, and therefore, both **2** and Ph₂S were expected if the dimer mechanism were in force. Also, it was predicted that there would be a dependence of the quantum yield for formation of **2**, ultimately leading to half the original value at high concentrations of Ph₂SO.

A series of photolyses were carried out in benzene solvent with 340 ± 12 nm excitation. At this wavelength, **1** has significant absorption, but the absorption of diphenyl sulfoxide is nearly negligible (Figure 5). In each solution, the initial concentration of **1** was kept at 2.10 mM, while the diphenyl sulfoxide initial concentration was 0, 32, 64, or 96 mM in different samples. Photolyses were carried out to low conversion (<10%) of **1**. Under these conditions, the yield of **2** was always >95% and the quantum yield was constant within experimental error at 0.0032. No Ph₂S was observed in any of the samples.

In another approach to testing the dimer mechanism, the photoreduction of **1** could be carried out under conditions where dimer formation would be severely restricted. Dilution and immobilization were the obvious strategies, so the reaction was run in a frozen organic glass. In addition, the polar nature of the sulfoxide function suggested that it ought to be tied up with hydrogen-bonding solvents to prevent any question of micro-aggregation. EPA glass at 77 K was chosen as the medium.

The strong phosphorescence of **2** at 77 K enables its detection at low concentration. The phosphorescence of **1** is to the red and significantly weaker, making the distinction between the

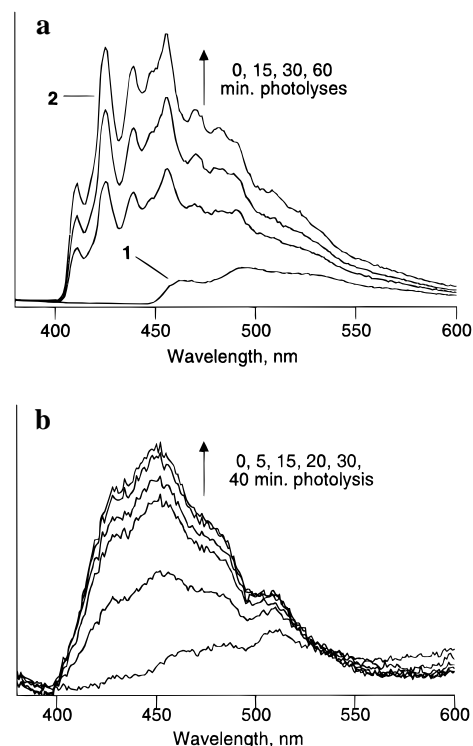


Figure 6. Phosphorescence spectra showing the grow-in of **2** as a function of photolysis time in EPA glass at 77 K. (a) 1 mM initial concentration of **1**; (b) 6×10^{-7} M initial concentration of **1**. The bump at about 520 nm is an artifact.

two straightforward.¹⁸ To demonstrate that phosphorescence could be used to monitor the progress of the photodeoxygenation of **1**, a 1 mM solution of **1** in EPA was prepared. It was deoxygenated by Ar flushing and then quick-frozen to 77 K, forming a clear glass in a 5 mm quartz NMR tube. A phosphorescence spectrum indicated only the presence of **1**. While remaining frozen, the solution was irradiated for 15 min with 300 nm bulbs of a Rayonet mini-reactor. A second spectrum showed the appearance of **2**. Repetition of this process showed continued grow-in of **2** over the course of an hour. The results of this experiment are shown in Figure 6a. The experiment was repeated with the initial concentration of the sulfoxide as low as 6×10^{-7} M, and the results of that series of measurements are shown in Figure 6b. In order to increase signal-to-noise, slit widths of the spectrometer were increased, so the resolution of the latter data is lower. There is no doubt, however, that the resulting spectra are due to **2**. The data shown in Figure 6b are completely untreated and show that the photochemical deoxygenation of **1** occurs under these conditions. The only ambiguity is whether the reaction proceeds to complete conversion, since quantitative analysis of such small, dilute samples by other means was difficult.

Another issue to address was the possibility of the formation of singlet molecular oxygen, O₂(¹Δ_g), in solution. It had been suggested that the observation of 2-cyclohexenol in the reaction mixture after photolysis of **1** in cyclohexene and subsequent NaI reduction was evidence of this event.³ Formation of an allylic hydroperoxide by the well-known ene reaction of singlet oxygen was the basis for this idea. We believed there might be other explanations for the appearance of the cyclohexenol. Moreover, it came to our attention that, after Posner's experiments, cyclohexene was found to be a good physical quencher of ¹O₂, but a lousy chemical quencher ($k_q = 1.6 \times 10^5$ M⁻¹

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s^{-1} , $k_{rxn} = 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$).²⁵ We sought to test, therefore, whether cyclohexene, under conditions similar to ours, could possibly act as a chemical trap for $^1\text{O}_2$. As a positive control, the oxidation of 1-methylcyclohexene, which is known as a good chemical quencher,²⁵ was examined first.

The allylic hydroperoxides generated by ene reactions with cyclohexene or 1-methylcyclohexene were not expected to be especially stable at ambient conditions. HPLC or GC detection was considered problematic due to stability, and NMR seemed problematic because we would be looking for a small amount of material in the presence of a large excess of alkene. Nonetheless, two broad, exchangeable singlets at 7.4 and 7.9 ppm were observed on generation of singlet oxygen in a 20% 1-methylcyclohexene solution in CDCl_3 at 0 °C. Consistent with expectations for hydroperoxide behavior, these peaks disappeared over the course of an hour and were replaced with a new exchangeable peak at 4.8 ppm. It was also observed that the solution, immediately post-photolysis, was capable of partially oxidizing solutions of dibenzyl sulfide to dibenzyl sulfoxide, also consistent with a hydroperoxide intermediate. After the peaks at 7.4 and 7.9 had disappeared, the solution was no longer capable of oxidizing the sulfide. Repetition of the experiments with cyclohexene did not generate similar new NMR peaks, nor did it cause the oxidation of dibenzyl sulfide.

If it is suggested that the fate of the O atom is other than formation of O_2 , one must account for it as best as possible. It was observed that much (and sometimes nearly all) of the lost oxygen could be accounted for in oxidation of the solvent, as we have reported.² In all of these experiments, degassing was accomplished by the freeze–pump–thaw method to ensure the most reliable reproducibility. Representative data, some of which are drawn from the previous publication,² are shown in Table 2.

The hydroxylation of 2-methylbutane was examined at several wavelengths: 254, 270, 290, 310, 330 nm. The hydroxylation selectivity was identical within experimental limits at all wavelengths.

In order to test the origin of the oxygen atoms in the oxidized substrates, [^{18}O]-**1** was prepared by analogy to literature methods involving exchange of H_2^{18}O into ordinary sulfoxides.^{26–30} Isotope enrichments were determined by analysis of appropriate GC–MS peaks. Dibenzothiophene sulfoxide containing 5.5% ^{18}O was produced. Photolysis of the [^{18}O]-**1** in benzene resulted in formation of phenol that contained 5.1% ^{18}O . This appeared to be identical within experimental error to the enrichment of **1**, but we cannot rule out that there was a small preference for ^{16}O .

Several experiments were carried out in which mixed solvents were exposed to **1** and light in order to determine the relative reactivity of these substrates. These reactions were carried out in the same fashion as for the previous oxidations. Products were quantified and compared to the mole fractions of the solvents to determine a *product-based* selectivity. Selected results are shown as Table 3. In the cases examined, there was no significant change in the chemoselectivity of oxidation of a given compound caused by the addition of the second oxidation substrate. All data shown are for multiple measurements at each of multiple concentration ratios. Also shown in Table 3 are

Table 2. Oxidation Products Observed on Photolysis of **1**

substrate (solvent)	total yield ^a (%)	products and rel ratio ^j
benzene	60–65%	phenol
cyclohexane	95–100%	cyclohexanol (2.1) cyclohexene (1)
cyclohexene	65–70 ^b	cyclohexene oxide (1.2) 2-cyclohexenol (1) 3-(3-cyclohexenyl)- cyclohexene (0.25)
2-methylbutane	40–45 ^c	tertiary alcohol (1) secondary alcohol (0.35) primary alcohols (0.25)
2,3-dimethylbutane	45–50 ^c	secondary alcohol (1) primary alcohols (0.55)
<i>cis</i> -4-octene ^e	50–60 ^d	<i>cis</i> -epoxide (1) <i>trans</i> -epoxide (1.1) alcohols (trace)
<i>trans</i> -4-octene ^e	~60 ^d	<i>trans</i> -epoxide (1) <i>cis</i> -epoxide (0.4) alcohols (trace)
allylbenzene	~30	epoxide (5.4) 1-phenylpropenol (2.8) cinnamyl alcohol (1)
<i>cis</i> - β -methylstyrene ^{f,g}	~20	<i>cis</i> -epoxide (1) <i>trans</i> -epoxide (2.8) alcohols (trace)
<i>trans</i> - β -methylstyrene ^{g,h}	~20	<i>trans</i> -epoxide (28) <i>cis</i> -epoxide (1) alcohols (trace)

^a Yields calculated relative to formation of **2**. ^b Possible cyclohexadiene not included, so actual yield is probably higher. Neither is the cyclohexene dimer, as small quantities of it are formed on photolysis of cyclohexene in the absence of **1**. ^c Possible olefinic products were not measured, so the actual total yield is likely higher. ^d The product yields for the octenes reflects only the epoxides. The actual yields were higher, including the allylic alcohols. ^e Carried out as 10% solutions of the alkene in dichloromethane. ^f Up to 15% *cis/trans* isomerization was observed by the end of the experiment. See text. ^g Carried out as 3% solutions of the alkene in dichloromethane. ^h $\leq 5\%$ *cis/trans* isomerization was observed by the end of the experiment. See text. ^j Ratios set against one compound arbitrarily set as 1. Ratios were generally reproducible to $\pm 10\%$, though a few were slightly more variant.

Table 3. Competitive Oxidation Experiments²

compd A	compd B	rate constant ratio (A/B) ^a	product selectivity ratio (A/B)
benzene	cyclohexene	0.021 ^b	0.019
benzene	cyclohexane	0.88	0.52 ^c
benzene	2-methylbutane		0.4
benzene (C_6H_6)	benzene (C_6D_6)	0.8	1.1 (0.9) ^c
cyclohexane (C_6H_{12})	cyclohexane (C_6D_{12})	6.0	6.5 (cyclohexanol) 6.2 (cyclohexene)

^a Rate constant ratios taken from ref 31 and have 15–20% error limits. Product ratio errors are of comparable magnitude. ^b Taken from Scaiano's values for benzene and cyclopentene and adjusted by 10% for the difference between cyclopentene and cyclohexene as determined in the gas phase.³⁷ Does not take into account cyclohexene, so the absolute number should be slightly lower. ^c 1.1 is the absolute product ratio. 0.9 is a selectivity ratio, adjusted for the ratio of recovery of phenol from C_6H_6 and C_6D_6 .

kinetic-based selectivities based on rate constants determined for $\text{O}(^3\text{P})$ quenching in solution by Bücher and Scaiano.³¹

A subset of the competitive oxidation experiments were isotope effect measurements. In this case, products were quantified by GCMS. Two cases were investigated, cyclohexane and benzene. The product isotope effects for cyclohexane were found to be 6.5 (cyclohexanol) and 6.2 (cyclohexene), in good agreement with the kinetic value of 6.0 observed by Bücher and Scaiano.

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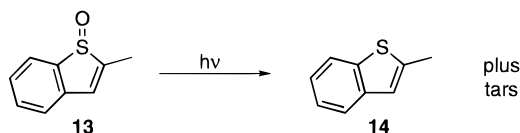
A product isotope of 1.4 for benzene was previously reported, which was in significant disagreement with the value of 0.83 derived from Scaiano's data. We have reexamined this data and now revise our earlier statements. Aside from the disagreement, the value we reported was disturbing. An inverse secondary isotope effect for hydroxylation of benzene is expected regardless of the detailed mechanism, if it is assumed that the product- and rate-determining step for both involve addition to the aromatic ring.

A necessary correction for the MS response factors of phenol and phenol-*d*₅ was not included in our original data. Furthermore, it was observed on careful rechecking that the fraction of phenol-*d*₅ relative to **2** in the reaction mixtures was consistently about 83% of that for ordinary phenol (again compared to **2**) when the two were photolyzed separately. Because we are not accounting for all the O atoms, and the isotope effect is near 1, this correction becomes important. It implies that between addition to the ring and formation of phenol, there is another isotope-dependent branching step, at which an intermediate commits to a pathway leading either to phenol or a different, unidentified product. Taking this into account, as well as the differing response factors, we now find that the actual product selectivity is 1.1, but that the selectivity of what we presume to be the first step, that is addition of O to the ring and disruption of the aromaticity is 0.9, in much better agreement with Scaiano's results.³¹

Discussion

Of the proposed dimer and sulfinyl mechanisms, the former has received more attention, and we address it first. It was proposed by Shelton on the basis of the products, and because many of the reactions were run with traditional triplet sensitizers.⁴ We have only addressed direct irradiation, since some of the sensitizers used almost certainly have insufficient triplet energies for energy transfer, implying an alternate sensitization mechanism.^{18,32} The triplet state was also implicated by Posner, who found that piperylene prevented the deoxygenation of Ph₂SO.³

The dimer mechanism was supported by a report of the photochemistry of several benzothiophene derivatives.⁵ Photolysis of most of these compounds leads mainly to [2 + 2] dimerization at the α,β-olefin, but 2-methylbenzothiophene sulfoxide **13** leads only to tars and a modest yield of the deoxygenation product. The quantum yield for formation of **14** was determined from 2–9 mM and was concentration dependent, with values ranging from about 0.03 to 0.08. A double-reciprocal plot of quantum yield *vs* concentration was linear and yielded a Stern–Volmer constant $k_r\tau_o$ of 4.3. These data, consistent with the dimer mechanism, was somewhat balanced by ambiguous results for diene quenching experiments, done on the assumption that the reactive state of **3** was a triplet.



The structural analogy between **1** and **13** makes it difficult to understand why there might be different mechanisms for the deoxygenation of each, and we have no reason to doubt the report of the photochemistry of **13**. However, the current results are definitively against the dimer mechanism for **1**, as we discuss immediately below. We must therefore allow for the possibility

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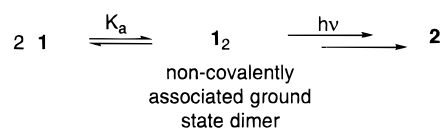


Figure 7. Dimer mechanism scheme based on preassociation in the ground state.

that either may be an exceptional case, and therefore restrict our conclusions at this time solely to compound **1** and not all deoxygenations.

The present data show that **1** does not undergo reduction *via* the dimer mechanism. More than the oxidations, which are merely unaccounted for, others of the results are contradictory with Figure 1. First among these are the quantum yields as a function of concentration, which, in contrast to the report for **13**, are invariant.

According to Figure 1 (assuming other ordinary processes and that dimer formation is irreversible), the quantum yield should be given by

$$\Phi_{\text{rxn}} = \Phi_{\text{T}} \cdot k_{\text{r}}[\mathbf{1}] \cdot (k_{\text{r}}[\mathbf{1}] + \Sigma k_{\text{d}})^{-1}$$

where Φ_{T} is the quantum yield of the reactive state and Σk_{d} represents all of the other unimolecular and pseudounimolecular decay rate constants for relaxation of the triplet. The insensitivity of Φ_{rxn} to $[\mathbf{1}]$ implies either that the scheme does not apply or that $k_{\text{r}}[\mathbf{1}] \gg \Sigma k_{\text{d}}$ throughout the whole region of concentrations. Since the lowest value of $[\mathbf{1}]_o$ was just under 10^{-3} M, the latter condition would require a lifetime of ³¹($\tau_o = [\Sigma k_{\text{d}}]^{-1}$) of at least 1 μs , assuming k_{r} approached 10^{10} M⁻¹ s⁻¹. While this is certainly reasonable, longer values would be required if k_{r} were smaller.

Let us assume $k_{\text{r}} \sim 10^{10}$ M⁻¹ s⁻¹ and $\tau_o \geq 1$ μs . In this case, it is expected that either dienes or O₂ would quench the reaction by providing an additional energy transfer decay pathway for ³**1**. Neither isoprene, cyclopentadiene, nor O₂ has that effect. Assuming smaller values for k_{r} only increases the required τ_o and, therefore, the vulnerability of ³**1** to quenching. A long-lived triplet ³**1** can be eliminated.

An alternate “rescue” for the dimer mechanism involves preassociation of the sulfoxides and static quenching (Figure 7). Here, the reactive state, singlet or triplet, is unimportant. The only requirement for a constant quantum yield over the range of $[\mathbf{1}]_o$ is that K_{a} is sufficiently large to tie most of the molecules up as dimers so that the concentration of **1**₂ tracks linearly with $[\mathbf{1}]$ over the range used in the experiments. This would require $K_{\text{a}} > 10^4$ M⁻¹. While such dimerization of sulfoxides is well known,^{33–35} Mislow showed that it is generally limited to dialkyl sulfoxides and is extremely solvent dependent, with ethanol and acetonitrile yielding monomeric species for butyl methyl sulfoxide even at concentrations approaching 100 mM. Diaryl sulfoxides were not found to be significantly associated, even in cyclohexane. Thus, both the nature of the substrate and the similarity of the quantum yields in solvents such as 2-propanol and cyclohexane argue strongly against this hypothesis.

Conversion of **1** to **2** at submicromolar concentrations at 77 K is, of course, inconsistent with the “dynamic dimer” mechanism of Figure 1. As the EPA glass contains significant quantities of ethanol, and the concentration of **1** is so low to

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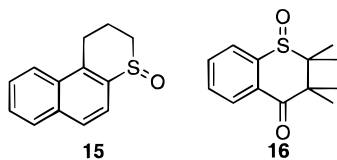
begin with, we assert that it is also inconsistent with a preaggregation mechanism.

Finally, the experiments in which **1** is photolyzed in the presence of diphenyl sulfoxide also argue against a dimer mechanism. It would have to be the case that there was at least a 2 order of magnitude selectivity of **1*** for itself in either self-quenching (dynamic case, Figure 1) or association (static quenching case, Figure 6).

As a second option, we consider the sulfinyl mechanism, which was proposed on the basis of CIDNP measurements during the photolysis of a series of aryl methyl sulfoxides **6**.¹¹ Deoxygenation accompanied α -cleavage chemistry. The NMR spectra of the product sulfides **11** showed polarization of the CH₃, but not of the aromatic ring. This was interpreted to signify that the sulfide was formed "as an immediate result of the primary photochemical event, by the escape path of [the radical pair **7/8**]."¹¹ The sequence in Figure 2, with transfer of an O atom from the sulfinyl radical **7** to another compound, presumably another radical, was used to account for these results.

Contrary to the dimer mechanism, which we cannot rule out for other cases, we believe the sulfinyl mechanism can be generally dismissed on energetic grounds, despite the CIDNP observations. The S–O bond of a sulfinyl radical is very strong. On the basis of Benson's estimate for the heat of formation of the phenylsulfinyl radical (13 kcal/mol; **7**, Ar = Ph)³⁶ and experimental values for the other relevant compounds,³⁷ a bond energy of *ca.* 102 kcal/mol is obtained for the S–O bond of PhSO•; the C–S bond is some 35 kcal/mol weaker. The transfer of the O atom from phenylsulfinyl to methyl is estimated to be endothermic by 12 kcal/mol. Further, epoxidation of ethylene by PhSO• (analogous to the alkene oxidations reported herein) is endothermic by about 17 kcal/mol!

The results in Tables 2 and 3 make it abundantly clear that some sort of powerful oxidizing intermediate is produced on photolysis of **1**. As argued in the Results, formation of 2-cyclohexenol from the photolysis of **1** in cyclohexene and reduction³ should no longer be considered good evidence for the presence of ¹O₂. In those original experiments positive qualitative tests for peroxide were also observed before the reduction step. A similar test, using **15**, did not yield a positive test for hydroperoxides, but the product(s) if any of cyclohexene oxidation are unreported.⁶ Similar results were obtained with **16**.⁷ Unspecified experiments to trap liberated oxygen from photolysis of **13** were also unsuccessful.⁵



We find that 2-cyclohexenol is produced on photolysis of **1** in cyclohexane but that the reduction step is not necessary. Indeed, photolysis under conditions nearly identical to those of Posner gave a yield quite consistent with his report.² Under those conditions (which include acetic acid as a cosolvent) in our hands, a small, but detectable, amount of epoxy-cyclohexane is observed. The small quantity may explain the discrepancy with Posner, who did not observe any.

We suggest two other mechanisms for consideration. The first is given in Figure 8, and will be called the "carbonyl-type"

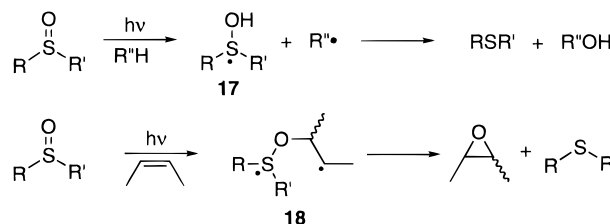


Figure 8. Reaction schemes involving carbonyl-type chemistry.

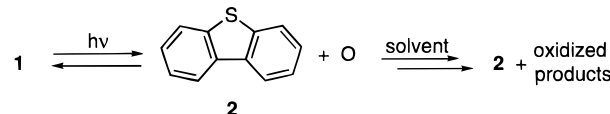


Figure 9. Deoxygenation of **1** by S–O bond cleavage.

class of mechanisms. It draws on an analogy with ketone photochemistry to suggest that the sulfoxide may abstract a hydrogen atom from solvent to produce the sulfinyl radical **17**. Oxidation of the solvent substrate occurs by transfer of the hydroxyl group to the solvent radical. The mechanism can be adapted for epoxidations by suggesting that (also like ketones) the sulfoxide can add to the double bond to produce biradical **18**, whose reactivity is dominated by epoxide formation with release of the sulfide. Because of the quenching results discussed above, this reactivity must be attributed to either a singlet or very short-lived triplet.

We do not favor the carbonyl-type mechanisms. First, evidence for hydrogen abstraction by sulfoxides is sorely lacking, though it has been suggested as a mechanism in several instances.¹⁵ Simply put, there are no published instances we know of in which transformations cannot be accounted for by α -cleavage as well as hydrogen abstraction. We have run several test cases designed to promote internal hydrogen abstraction and see products that could be attributed to it unambiguously. (Among these, for instance, are compounds designed to undergo "Norrish type II" cleavage.) None of these reactions have been observed.¹³

Furthermore, the quantum yields for formation of **2** in solvents whose reactivity is as diverse as 2-propanol, benzene, acetonitrile, and toluene are nearly identical. Even that in Freon 113 is within 20% of those previously mentioned. The mechanism ought to account better for similar quantum yields in solvents with such different hydrogen atom donation ability. While it is possible to rationalize an increased reactivity in cyclohexene, and even tetrahydrothiophene (perhaps electron transfer), it is hard to understand the presence of DMSO in the "high quantum yield" group of solvents for this class of mechanisms.

As Wagner demonstrated so elegantly for hydrogen abstraction reactions, arguing about mechanism from quantum yields for product formation can be dangerous, as intermediates can be prone to returning to starting materials, giving an extra efficiency-determining step.^{19,38,39} While acknowledging that possibility, this group of solvents seems diverse enough to make such a leap.

We propose one further possibility, with which we believe all the experiments are consistent. Figure 9 shows a mechanism in which the excited state sulfoxide undergoes S–O cleavage. The result is generation of an O atom, which, for energetic reasons, must be in its ground state O(³P). The O atom is ultimately trapped by reaction with solvent or **2**. We do not rule out some sort of noncovalent complex that might involve

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interaction of the oxygen atom with the π system of **2** or an excited state whose reactivity merely effectively mimics $O(^3P)$.

An important issue is the strength of the S–O bond and its relationship to the excited state energies. Fluorescence and phosphorescence measurements place the singlet and triplet energies of **1** at 82 and 61 kcal/mol, although there is some variation with solvent.¹⁸ Experimental heats of formation are available for many sulfides, but only a few sulfoxides: DMSO, a few other simple dialkyl sulfoxides, and Ph_2SO . From these, and the heat of formation of $O(^3P)$, bond energies of 85–90 kcal/mol can be established.⁴⁰ These are several kcal/mol more than what is available from the relaxed singlet of **1** and make the dissociation mechanism appear unlikely, especially at 77 K. However, in a recent computational study,⁴¹ it was shown that the aromaticity of **2** effectively lowers the S–O bond energy of **1** down to the range of 74–78 kcal/mol, now well under the energy of the singlet excited state. (This bond weakening effect is larger and larger still for benzothiophene sulfoxide and thiophene sulfoxide, respectively.)

The pattern of quantum yields is qualitatively understood as a reflection of the reactivity of the solvent with the nascent O atom. There exists a competition between recombination with **2**, diffusive separation, and reaction of the O atom with solvent. Intuitively, it is reasonable to expect that tetrahydrothiophene, cyclohexene, and DMSO would be qualitatively more reactive with $O(^3P)$ than the other substrates, as one anticipates reactions analogous to an electrophilic triplet carbene. An increased reactivity of the solvent with $O(^3P)$ then leads to an increase in the observed Φ_{rxn} .

We are not aware of any clean method to generate $O(^3P)$ in solution, aside, perhaps, from photolysis of **1**. This means ordinary chemical tests such as those used to probe for 1O_2 are not available. While atomic oxygen, due to its importance in combustion and atmospheric chemistry, has been investigated repeatedly in the gas phase, data regarding its solution phase reactivity are very limited, particularly with regard to organic substrates. Nonetheless, the products in Table 2 are consistent with intuitive expectations for $O(^3P)$, which we would expect to behave like an electrophilic triplet carbene. All of the observed products can be explained on the basis of a reaction sequence that begins with hydrogen abstraction or addition of O to an olefin (or arene).

The hydroxylation reactivity reported in Table 2 is similar to that observed for Cytochrome P-450 models, much of which can be described in terms of Groves' "oxygen rebound" mechanism.^{42–50} Essentially, hydroxylations are described as a net hydrogen abstraction followed by delivery of a hydroxyl radical to the substrate radical, as would be anticipated for a true triplet oxene. (In contrast to the current results, however, the P-450 model epoxidations are usually stereospecific.)

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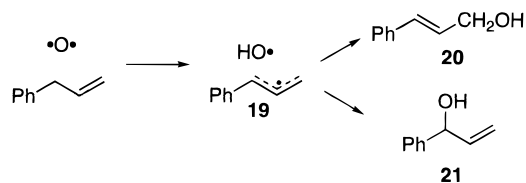
(49) Groves, J. T.; Gross, Z.; Stern, M. K. *Inorg. Chem.* **1994**, *33*, 5065–5072.

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Photolysis of N_2O in hydrocarbon solutions with 185 nm light produces mainly $O(^1D)$.⁵¹ A very slight selectivity for secondary or tertiary hydroxylation *vs* primary was attributed to minor amounts of ground-state $O(^3P)$. Hydroxylation of *cis*-decalin also proceeded with retention of configuration (95% at 0 °C). All of these point to direct insertion, in contrast to the results in Table 2. Once the number of hydrogens are taken into account, there is approximately 1 order of magnitude selectivity for secondary hydroxylation over primary and a similar, if slightly lower, preference for tertiary hydroxylation over secondary. Taken with the isotope effect of about 6 observed for both products of cyclohexane, a stepwise oxidation pathway of hydrogen abstraction followed by recombination (or disproportionation) is suggested.

Similarly, the partial randomization of stereochemistry in the epoxidation of octene and β -methyl styrene isomers suggests that the reaction is stepwise, though the intermediate still has a fairly short lifetime, as gauged by the incomplete equilibration of stereochemistry. Significant *cis/trans* isomerization of the alkene under the reaction conditions was observed for *cis*- β -methylstyrene, but for none of the others. Even in that case, however, the percentage of *trans*-epoxide far exceeded the percentage of *trans*-olefin.

For all the alkenes, epoxidation is favored over hydroxylation. However, one example in particular deserves attention. In the photolysis of **1** in allylbenzene, both cinnamyl alcohol and **21** were identified. Assuming for the moment that the initial oxidant is $O(^3P)$, this is rationalized by the presence of a discrete allyl-type radical **19**.



We presume that benzene is oxidized to phenol by stepwise addition of O to the ring, forming benzene oxide. The latter is thought to rearrange to phenol under the reaction conditions. The small isotope effects are consistent with the initial step of addition to the ring. Similar isotope effects were recently obtained for the hydroxylation of xylene isotopomers by microsomal cytochrome P-450.⁵² The ^{18}O -labeling experiments clearly show that the O atom derives from **1**. We find no direct evidence of benzene oxide or of oxepin. However, it is well known that benzene oxide/oxepin readily isomerizes to phenol (sometimes along with other products) in the presence of Brønsted acid, heat, or light.^{53,54} The less than quantitative yield of phenol may reflect undetected products derived from other processes available to the benzene oxide/oxepin. Indeed, the percentage recovery of phenol differed for benzene and benzene- D_6 , directly indicating an isotope-dependent branching prior to phenol formation.

For comparison to previous results with $O(^3P)$, the best data are the rate constants of Bücher and Scaiano,³¹ who generated $O(^3P)$ by photolysis of pyridine *N*-oxide. This compound

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predominantly undergoes rearrangement processes, but it has been shown that a small fraction of the molecules dissociate to pyridine and $O(^3P)$.^{55,56} (It should also be noted that this also represents a precedent for X–O photochemical cleavage from hypervalent organic compounds.) Rate constants (only) were determined for the reaction of $O(^3P)$ and a variety of substrates in organic solution, ranging from $2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for Br^- (as Bu_4N^+) to $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for chloroform and dichloromethane. Interestingly, they showed that $O(^3P)$ is a significantly more selective reagent than HO, as judged by rate constants, which tend to cluster between 10^9 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for HO. Product competition studies are more difficult for rate constant differences of more than about 2 orders of magnitude, but the cases shown in Table 3 are consistent with the kinetic data.

Regarding the photoactive state of **1**, the quenching experiments are consistent with either a short lived (unquenchable) triplet or a singlet state of **1**. If an S–O bond cleavage mechanism is correct, an excited state energy of the order of 80 kcal/mol or greater is necessary. This precludes the phosphorescent triplet of **1**, whose triplet energy is much lower.¹⁸ If reactivity is out of the lowest excited singlet of **1**, whose fluorescence energy is about 82 kcal/mol, then we must recognize that we are postulating a formally spin-forbidden process. On the other hand, the quantum efficiencies are quite low, which may be consistent with this notion. Another possibility is that a short-lived upper triplet state is involved. The unusual dependence of the quantum yield on the excitation wavelength may support this idea, particularly in combination with the observation that the hydroxylation selectivity is independent of the excitation wavelength. The latter suggests (but does not prove) that a common oxidizing intermediate is produced, simply with a higher efficiency with higher energy excitation.

It should be emphasized that our data are merely *consistent with* formation of $O(^3P)$. We have made no observation that directly implies the existence of this or any other short-lived intermediate. Nonetheless, it is exceedingly clear that photolysis of **1** produces a transient of some sort that is a very powerful oxidation agent. Circumstantial evidence described herein

suggests that the oxidation agent may be $O(^3P)$ or a solvated complex with similar reactivity.

Summary

Photolysis of dibenzothiophene sulfoxide produces dibenzothiophene in very high chemical yield and low quantum yield. The quantum yield is independent of sulfoxide concentration. This and other experiments rule out the formation of any sort of sulfoxide dimer as part of the mechanism for formation **2**. A proposed mechanism for deoxygenation based on O-atom transfer by sulfinyl radicals is ruled out on energetic bases. Mechanisms based on direct interaction between solvent and the excited state of **1** in reactions analogous to carbonyl photochemistry cannot be ruled out, but seem unlikely due to the pattern of quantum yields in different solvents.

In addition to **2**, photolysis of **1** produces a species that is capable of oxidizing benzene to phenol and hydroxylating alkanes. The yield of such oxidized products ranges from modest to nearly quantitative. The pattern of reactivity is consistent with intuitive expectations for $O(^3P)$ or a similar substance, and it is speculated that this may be the mechanism for formation of **2**. Dehydrogenation of alkanes has also been demonstrated. The stepwise nature of the hydroxylation reaction has been demonstrated by formation of both alcohols derivable from a 1-phenylallyl radical. The stepwise nature of epoxidations is demonstrated by the partial loss of stereochemistry in acyclic substrates. Product competition studies are consistent with kinetic comparisons to rate constants for removal of $O(^3P)$, as determined by Scaiano.

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