

Electrophilic Oxidant Produced in the Photodeoxygenation of 1,2-Benzodiphenylene Sulfoxide

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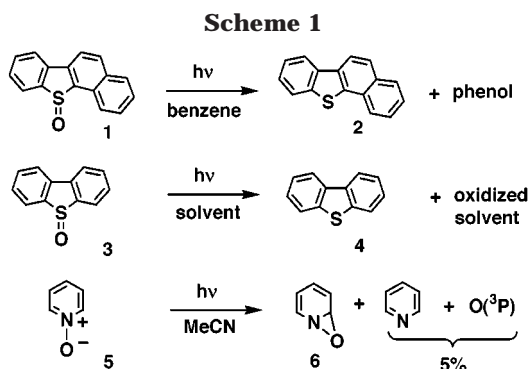
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We report that the photodeoxygenation of 1,2-benzodiphenylene sulfoxide, **1**, generates an intermediate capable of oxidizing the solvent benzene to phenol. The reactivity of the intermediate was probed with various substrates (2-methylbutane, chloride ion, and para-substituted aryl sulfides). The intermediate produced in the sulfoxide photodeoxygenation displays an electrophilic oxidation chemistry. Our data on **1** contrast with the behavior of hydroxyl radical but resemble the chemistry observed for gas-phase atomic oxygen [O(³P)] and for solution-phase photodeoxygenations of dibenzothiophene sulfoxide, **3**, and pyridine *N*-oxide, **5**. Correlations are made between the ionization potential of the acceptor molecules and the logarithm of the relative rate constants in order to advance the idea that the oxidizing agent of the title reaction may be solution-phase O(³P).

Introduction and Background

The first reports of photoinduced deoxygenation of aromatic sulfoxides came approximately 25 years ago.^{1,2} Since this time Jenks and co-workers^{3,4} suggested a mechanism for the photodeoxygenation of dibenzothiophene sulfoxide (**3**), which suggested that along with dibenzothiophene (**4**) an intermediate was produced capable of oxidizing the solvent. The intermediate generated in the photodeoxygenation of **3** was tentatively assigned as atomic oxygen O(³P) or a closely related noncovalent complex. This assignment was based on the oxidation chemistry, on comparison with known rate constants of O(³P), and on the quantum yield data (Scheme 1).

The gas-phase chemistry of singlet-excited (O(¹D)) and triplet-ground-state atomic oxygen (O(³P)) is known but little is known of the condensed phase chemistry. The gas-phase reactivity of O(³P) is established;⁵ however, the potential value of O(³P) as a reagent in organic chemistry and biochemistry remains unknown. The lack of information partly reflects the scarcity of sources of O(³P) in solution. Numerous studies have addressed metal-dioxo species, superoxides, and other activated molecular oxygen species, but none are known to produce O(³P). Elegant work of Scaiano⁶ suggest that the formation of O(³P) in acetonitrile solution occurs upon irradiation at 308 nm of pyridine *N*-oxide (**5**). The assignment of O(³P) was based on the fact that the experimental method allowed one to monitor the product of its reaction with the solvent, acetonitrile oxide, and also by comparisons



with gas-phase data on O(³P). Only minor amounts of O(³P) appear to be formed (~5%) in the photolysis of **5** compared to the photochemically rearranged product, oxaziridine (**6**).

Gas-phase methods that produce O(³P) are not readily compatible with solution phase methods. Gas-phase mercury triplet photosensitized decomposition of N₂O indicates formation of O(³P) based on energetics;^{5,7} however, a common method for spectroscopic detection of O(³P) requires monitoring its vacuum UV laser-induced fluorescence (LIF) signal at ~130 nm.⁸ The disadvantage of current methods that generate O(¹D) or O(³P) in solution, include (1) harsh photolysis conditions (e.g., [⁶⁰Co] γ -ray irradiation of liquid water⁹ or alkaline H₂O₂ solutions,¹⁰ 185 nm photolyses of N₂O¹¹), (2) the presence of other reactive intermediates (e.g., oxoanions and oxoacids,¹² photodecomposition products of NO₃⁻¹³), or (3)

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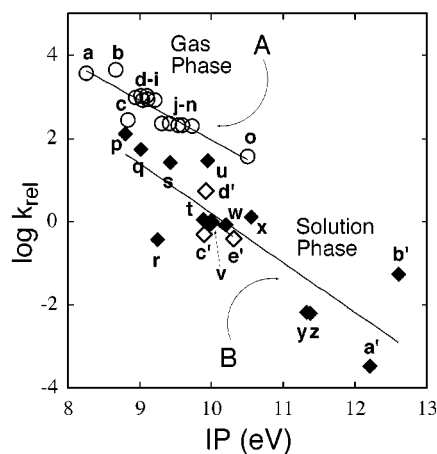


Figure 1. Correlation of $\log k_{\text{rel}}$ for oxidation with adiabatic ionization potentials of the acceptor molecules. Oxidation of alkenes (A, slope = -0.950 eV^{-1} , $r^2 = 0.898$; ref 5; **a** = 2,3-dimethyl-2-butene; **b** = 1-methyl-1-cyclohexene; **c** = 2-methyl-2-butene; **d** = cyclohexene; **e** = cyclopentene; **f** = 2-pentene; **g** = *trans*-2-butene; **h** = *cis*-2-butene; **i** = 2-methyl-2-propene; **j** = 1-hexene; **k** = 1-pentene; **l** = 3-methyl-1-butene; **m** = 1-butene; **n** = propene; **o** = ethene) with gas-phase $\text{O}(^3\text{P})$ atoms. Oxidation of substrates from the photolysis of **5** (B, slope = -1.193 eV^{-1} , $r^2 = 0.845$, ref 6; **p** = trimethyl phosphite; **q** = cyclopentene; **r** = pyridine; **s** = 1-octyne; **t** = cyclohexane; **u** = 1-octene; **v** = benzene; **w** = *n*-pentane; **x** = cyclopentane; **y** = dichloromethane; **z** = chloroform; **a'** = acetonitrile; **b'** = methane) in acetonitrile solution and **3** (C (not labeled), slope -1.377 eV^{-1} , $r^2 = 0.515$, refs 3,4; **c'** = cyclohexane; **d'** = cyclohexane- d_{12} ; **e'** = 2-methylbutane) in alkane solutions.

the need for high-pressure (e.g., SF_6)¹⁴ or low temperature (N_2)¹⁵ solvents. We now report a much cleaner oxidation method. Mildly energetic 385 nm light can initiate the deoxygenation of 1,2-benzodiphenylene sulfoxide (**1**), which generates an intermediate capable of oxidizing the solvent benzene to phenol. The reactivity of the intermediate was probed with various substrates (2-methylbutane, chloride ion, and para-substituted aryl sulfides) and is found to have the electrophilic oxidation chemistry that is expected of atomic oxygen [$\text{O}(^3\text{P})$] in solution.

Results and Discussion

In our initial efforts, we sought a basis to compare established gas-phase $\text{O}(^3\text{P})$ reactions with solution phase methods that potentially yield $\text{O}(^3\text{P})$. A similarity emerges when comparing molecular oxidations from (1) gas-phase $\text{O}(^3\text{P})$,⁵ and (2) solution phase **3**- and **5**-photodeoxygenations^{3,4,6} (Figure 1). A linear relationship is found when the logarithm of the relative rates, taken from refs 4–6, are plotted versus ionization potentials of their respective acceptor molecules.¹⁶ The data falls into two groups; one for the gas phase (Figure 1A) and the other for the solution phase (Figure 1B,C). Both rates correlate with the ionization potential and have about the same slope.

Since gas-phase studies have established the electrophilicity of $\text{O}(^3\text{P})$ by correlating such rate dependencies on acceptor molecule ionization potentials,^{17–20} we reasoned that a similar correlation could add confidence to the suggestion that **3** and **5** may lose oxygen to yield $\text{O}(^3\text{P})$ in solution. The quality of the data in Figure 1B,C does not constitute a “proof” of the $\text{O}(^3\text{P})$ intermediate in solution; however, it does provide strong circumstantial evidence.

Solvent Oxidation. In the present work, we focus on **1**, which is similar to Jenks' compound **3**^{3,4} except for the additional fused benzene ring. This change moves the second UV band maximum from 321 to 343 nm, and enables us to induce similar chemistry at lower energies. Compound **1** is a candidate for unimolecular $\text{S}=\text{O}$ cleavage because of a comparable excited state ($\sim 75\text{--}78 \text{ kcal/mol}$, from the UV–visible spectrum) and sulfur–oxygen bond dissociation energy (76.8 kcal/mol, from UB3LYP/6-31G(d)//B3LYP/3-21G calculations).²¹ In the presence of 385 nm light in argon-saturated benzene at room temperature, **1** (2–6 mM) deoxygenated to give phenol and 1,2-benzodiphenylene sulfide (**2**). Deoxygenation of **1** also proceeded in the presence of 300, 320, 340, or 365 nm light. Products that would indicate disproportionation (1,2-benzodiphenylene sulfone) or sulfur monoxide extrusion (2-phenylnaphthalene) were not detected. At 8% conversion the ratio of phenol:**2** is 0.81 by gas chromatographic analysis. Identical results were obtained in acetonitrile:benzene (2.9 M:9.5 M) mixtures at room temperature. Photolyses were conducted with a 75-W Xenon lamp focused on a monochromator (linear dispersion equal to $\sim \pm 12 \text{ nm}$). Control experiments demonstrate that benzene is inert to **1** in the absence of light. We next wanted to learn if this hydroxylation exhibits any selectivity.

Alkane Hydroxylation. Photodeoxygenation of **1** (4 mM) in acetonitrile solution containing 0.687 M 2-methylbutane demonstrated a regioselective hydroxylation yielding 2-methyl-2-butanol (71%), 3-methyl-2-butanol (19%), 2-methyl-1-butanol (4%), and 3-methyl-1-butanol (5%). The ratios of alcohol products observed from the photodeoxygenation of **1** are similar to those reported from the photodeoxygenation of **3**.^{3,4} One might suggest that the selectivity for the formation of alcohol products in the photodeoxygenation of **1** and **3** is derived from a recombination of a caged hydroxyl radical–alkyl radical pairs in a stepwise carbon–hydrogen bond insertion process. Gas-phase alkane hydroxylations have shown that $\text{O}(^3\text{P})$ reacts selectively at tertiary C–H,²² whereas $\text{O}(^1\text{D})$ ¹¹ and OH radicals^{6,23} show little if any selectivity.

Hypochlorite Ion Formation. These studies are the first to indicate that hypochlorite ion can form from a sulfoxide photodeoxygenation reaction in the presence of

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(21) It is not known whether $\text{S}=\text{O}$ cleavage can originate from the singlet-excited state of **1**. While the UB3LYP/6-31G(d)//B3LYP/3-21G calculated energy split of the singlet-ground and triplet state (63.2 kcal/mol) is below the BDE, this does not rule out possible $\text{S}=\text{O}$ cleavage from a vibrationally excited triplet state.

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chloride ion. Competitive kinetic studies were conducted with the 365 nm photochemical decomposition of **1** (2 mM) with tetrabutylammonium chloride (38 mM) in acetonitrile:benzene (3.8 M:8.4 M), which produced **2**, hypochlorite ion (OCl^-), and phenol. After photolysis, the mixture was stirred overnight, and hypochlorite ion was detected as the chlorinated adduct of added 1,3,5-trimethoxybenzene (~ 150 mM) using chemistry previously established by Foote.²⁴ The product ratio of OCl^- (as 2-chloro-1,3,5-trimethoxybenzene) was found to be 191 ± 30 times that of phenol, which is similar to the kinetic ratio (200:1, chloride ion:benzene) derived from the absolute rate constants for removal of $\text{O}(\text{^3P})$ in acetonitrile.^{6,25} The above similarity represents a comparison between product- and kinetic-based selectivities. Phenol yields were determined in our product study but not in Scaiano's kinetic study.⁶ The reactivity of the intermediate in the photodeoxygenation of **1** is unlike that of OH radical because OH radicals are known to react with chloride ion and benzene with a similar preference $\sim 1:1.1$.^{6,23} The preference for a reaction with an electron rich substrate is indicated here for the first time in the photodeoxygenation of an aromatic sulfoxide.

Hammett Studies. We further demonstrate the preference of the intermediate for an electron rich substrate via a Hammett trapping study of the sulfoxide photodeoxygenation. Addition of electron-donating groups on the substrate leads to enhanced relative reaction rates toward the intermediate formed in the photodeoxygenation of **1** and **3**. Compound **1** was selectively irradiated ($h\nu = 365$ or 385 nm; $2-8$ mM) in the presence of a series of diaryl sulfides [$(p\text{-X-C}_6\text{H}_4)_2\text{S}$, where X = OMe, Me, H, and Cl; $4-9$ mM] in argon-saturated acetonitrile solutions. Control reactions demonstrate that the aryl sulfides do not react with **1** in the absence of light. The products formed are **2** and the corresponding aryl sulfoxides, $(p\text{-X-C}_6\text{H}_4)_2\text{SO}$. Maintaining $<10\%$ conversion of the reaction components, the ratios k_x/k_H determined from the slopes of plots of $[(p\text{-X-C}_6\text{H}_4)_2\text{SO}]$ versus $[(\text{C}_6\text{H}_4)_2\text{SO}]$ yielded evidence for an electrophilic oxidant (Hammett $\rho = -1.57 \pm 0.13$, $r^2=0.975$). Moreover, in an analogous experiment, we demonstrated that the photodeoxygenation of **3** with 350 nm light in the presence of the same series of diaryl sulfides yielded a Hammett plot with a ρ value = -1.48 ± 0.11 ($r^2 = 0.956$). These data suggest that the intermediate derived from the photodeoxygenation of **1** and **3** are similar or identical. The magnitude of the reaction constants ($\rho = \sim -1.5$) implies a build-up of positive charge on the $(p\text{-X-C}_6\text{H}_4)_2\text{S}$ sulfur in the transition state.

Another measure of the character of the intermediate comes from comparing the relationship between the relative rate constants, and the $(p\text{-X-C}_6\text{H}_4)_2\text{S}$ ionization potentials. A plot of the logarithm of the relative rates of **1** and **3** versus the adiabatic ionization potentials of the aryl sulfides^{16,26} revealed a linear dependence (Figure 2A,B). These observations are very similar to those reported in the gas-phase $\text{O}(\text{^3P})$ oxidations of MeSSMe ,

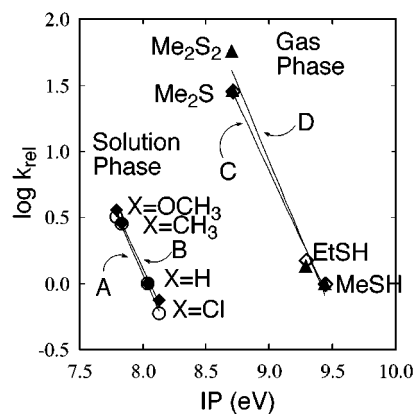


Figure 2. Correlation of $\log k_{\text{rel}}$ with the adiabatic ionization potentials for the oxidation of sulfur compounds. Oxidation of para-substituted aryl sulfides (X = OMe, Me, H, Cl) in the photodeoxygenation of **1** (A, open circles, slope = -2.15 , $r^2 = 0.998$) and **3** (B, solid diamonds, slope = -2.05 , $r^2 = 0.997$) in MeCN solution. Oxidation of MeSSMe , Me_2S , EtSH , and MeSH with gas-phase $\text{O}(\text{^3P})$: C (open diamonds, slope = -2.05 , $r^2 = 0.996$, ref 18) and D (solid triangles, slope = -2.31 , $r^2 = 0.988$, ref 19,20).

Me_2S , EtSH , and MeSH (Figure 2C,D).¹⁸⁻²⁰ The rate constants are well correlated with the ionization potentials for the solution and gas-phase data. The substantial negative slopes in the IP plots provide evidence of partial electron transfer or charge transfer between the electron rich aryl sulfide additives and the electrophilic oxygenating intermediate. Our data on **1** is reminiscent of the oxygenating character of high-valent iron porphyrins.²⁷

The observation of similar slopes between Figure 2A,B and 2C,D provides limited evidence for $\text{O}(\text{^3P})$ as a common intermediate because it is conceivable that the solution-phase systems bear a rate dependence on the ionization potential in a bimolecular reaction between the excited state of **1** or **3** and the aryl sulfide acceptor. This could especially be true because, by analogy, sulfoxides are capable of forming dimeric structures, although elevated concentrations are generally required.²⁸⁻³⁰ The relative changes in the ionization potential may be attributable to solvation given the abscissa of the plot is the ionization potential of the molecule. The coincidence of the gas and solution phase slopes³² (Figure 2A,B and 2C,D) may be fortuitous; however, we believe that the data point to an identical reactive intermediate, $\text{O}(\text{^3P})$.

Conclusion

The properties of the photodeoxygenation of **1** have been examined in order to investigate the nature of the possible intermediate. An intermediate is generated which is capable of oxidizing benzene, chloride ion, 2-methylbutane, and para-substituted aryl sulfides. With the above data, it is not yet possible to prove absolutely the existence of $\text{O}(\text{^3P})$ in solution. However, the relative

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(25) Interestingly, the extent of electron transfer between chloride ion and $\text{O}(\text{^3P})$ may be significant since Scaiano's pyridine *N*-oxide system determined the rate of reaction to be above diffusion control.⁶

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reactivity and similarity to gas-phase $O(^3P)$ and solution systems **3** and **5** suggests $O(^3P)$ as a potential short-lived intermediate formed in the UV deoxygenation of **1**.

Experimental Section

General Aspects. 1,2-Benzodiphenylene sulfide (Aldrich 99%), dibenzothiophene sulfide (Aldrich 99%), phenol (Aldrich 99%), tetrabutylammonium chloride (Fluka 99%), 2-methylbutane (anhydrous, Aldrich 99%), 2-methyl-2-butanol (Aldrich 99%), 3-methyl-2-butanol (Aldrich 98%), 2-methyl-1-butanol (Aldrich 99%), 3-methyl-1-butanol (Aldrich 99%), sodium hypochlorite (Aldrich 4% aqueous solution), 1,3,5-trimethoxybenzene (Aldrich 99%), biphenyl (Aldrich 99%), diphenyl sulfoxide (Aldrich 96%), and acetonitrile (anhydrous, Aldrich 99.8%) were used as received. The purity of the reagents was checked by GC or GC/MS prior to use. Diphenyl sulfide (Aldrich 99%) was distilled under reduced pressure (bp 124 °C/6 mmHg). Benzene (anhydrous, Aldrich 99.8%) was distilled over P_2O_5 . Compounds **1** and **3** were synthesized and purified using a literature method.³¹ Relative concentrations of **1–4**, phenol, 2-methyl-2-butanol, 3-methyl-2-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-chloro-1,3,5-trimethoxybenzene, and the para-substituted aryl sulfoxides (*p*-X-C₆H₄)₂SO were determined by reference to calibration curves constructed from authentic samples. Gas chromatographic data were collected on one of two gas chromatographs, a Hewlett-Packard GC/MS instrument consisting of a 5890 series GC and a 5988A series mass selective detector, or on a Shimadzu-17A autosampler capillary gas chromatograph.

Sulfoxide photodeoxygenation reactions were carried out using 1.5 mL airtight GC vials or 5-mm NMR tubes at room temperature and irradiation with a 75-W Xenon Model L-201 Arc lamp (Photon Technology International) focused on a tunable monochromator to obtain monochromatic light over the range 280–400 nm. A typical experiment was conducted in a 1-mL solution of spectral grade benzene, which contained 3 mM **1** and 5×10^{-4} M biphenyl as an internal standard. Often cosolvents were used, such as acetonitrile:benzene (2.9

M:9.5 M) mixtures. Argon was flushed through the reaction mixtures for 15–30 min prior to irradiation. Phenol was detected in the benzene and acetonitrile:benzene solutions by gas chromatography when **1** was irradiated with 300, 320, 340, 365, or 385 nm light. Alkane hydroxylations were conducted in Ar-saturated acetonitrile solutions containing 4 mM **1**, 5×10^{-4} M biphenyl as an internal standard, and 0.687 M 2-methylbutane using 365 or 385 nm light. Chloride ion trapping was conducted by irradiating Ar-saturated acetonitrile:benzene (3.8 M:8.4 M) solutions with 365 nm light containing 4 mM **1**, 5×10^{-4} M biphenyl as an internal standard, and 38 mM tetrabutylammonium chloride. After photolysis the reaction mixture was stirred overnight and hypochlorite ion detected as the chlorinated adduct of added 1,3,5-trimethoxybenzene (~150 mM).²⁴ The aryl sulfide Hammett studies were conducted in 1-mL GC vials in Ar-saturated acetonitrile solutions containing 4 mM **1**, 5×10^{-4} M biphenyl as an internal standard, and 4 mM Ph₂S and 4 mM (*p*-X-C₆H₄)₂S and irradiating with 365 or 385 nm light. Hammett studies were conducted in an identical fashion with **3** except that 350 nm light was used. In all experiments the irradiation times were selected (~2–3 h) in order to ensure less than 10% of any reaction component. The concentrations of products were determined in the reaction mixtures immediately after photolysis by gas chromatography.

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