

Gauging the Significance of Atomic Oxygen [O(³P)] in Sulfoxide Photochemistry. A Method for Hydrocarbon Oxidation

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Received November 2, 2002

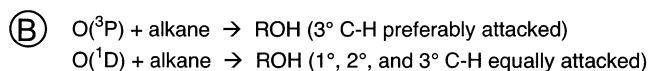
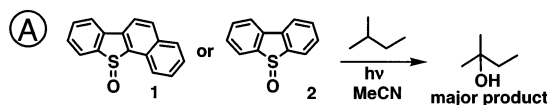
A liquid-phase photolysis of 1,2-benzodiphenylene sulfoxide, **1**, and dibenzothiophene sulfoxide, **2**, was used to generate atomic oxygen [O(³P)] or an equivalent active oxygen species. The reaction for sulfoxide photodeoxygenation was similar to a microwave discharge method for generating O(³P) atoms in the condensed phase (Zadok, E.; Rubinraut, S.; Mazur, Y. *J. Org. Chem.* **1987**, *52*, 385–90). Sulfoxide photodeoxygenation is a potentially clean method for O(³P) production compared to the microwave discharge method. With Argon purging of the sulfoxide sample before photolysis, the method can preclude a secondary oxidation process involving molecular oxygen. Our study focused on the results of oxidation products in the reaction of styrene, **3**, and on the dependence of substrates that provided an opportunity to vary the electronic and steric effects. The sulfoxide photochemistry is rationalized with the primary formation of O(³P) in which a charge-transfer interaction between O(³P) and substrate precedes oxidation. Functionalization of hydrocarbons takes place under mild photolysis conditions of **1** and **2**, which leads to an interesting possibility for the synthetic use of atomic oxygen, O(³P). Alkanes give principally alcohols. Alkenes give principally epoxides and ketones. For comparison, hydroxyl radicals are more reactive and less selective toward hydrocarbons compared to O(³P) atoms. On the other hand, O(³P) atoms balance reactivity and selectivity and involve the oxidation of inert alkanes typically inaccessible to peracid, dioxirane, ozone, and singlet molecular oxygen chemistry. The findings from this study may be useful to those interested in generating high-value oxygenated compounds from readily available petroleum components.

Introduction

In the presence of light, sulfoxides **1** and **2** can react with alkanes to afford alcohols.^{1–3} Oxygen is introduced in a selective manner in 2-methylbutane (Scheme 1A). The mechanism is postulated as the loss of oxygen from sulfoxide to yield atomic oxygen [O(³P)] or an equivalent active oxygen species capable of oxygen transfer to the hydrocarbon.^{1–3} Sulfoxide photodeoxygenation methods may enable one to address questions about atomic oxygen in the condensed phase. Building a context for the chemistry would be desirable. Atomic oxygen is a selective agent in the ground state, O(³P), and a nonselective agent in the excited state, O(¹D) (Scheme 1B).^{4–6}

The selective oxidation of hydrocarbon bonds is a seminal and longstanding problem in organic chemistry.⁷ A reagent, such as atomic O(³P), that possesses the ability to transform hydrocarbon bonds to oxygenated functional groups would have useful applications. Yet despite the

SCHEME 1



previous work on condensed phase O(³P) atoms,^{5,8–11} and despite its potential as an oxidizing agent,^{12–14} organic chemists do not often view O(³P) atoms as a reagent for synthetic transformations. Little is known of O(³P) atoms in the condensed phase compared to the gas phase. The reaction may be complicated by solvent effects. Few studies have brought together results on condensed phase O(³P) atoms, which address questions about the influence of solvent. Complexes or ions are commonly encountered

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in solution studies of sulfur,¹⁵ chlorine,^{16,17} and fluorine atoms.¹⁸ One would expect that complexation and ionization pathways of O(³P) may differ in solution compared to the gas phase.^{19,20}

We sought to establish the mechanistic criteria to learn of a possible sulfoxide method to generate O(³P) atoms or an equivalent active oxygen species. Microwave discharge methods generate O(³P), but often in the presence of other reactive species, such as O(¹D), ¹O₂, and O₃.^{8,21,22} In developing the research problem on sulfoxide photochemistry, it was important to choose a system whose solution phase O(³P) reaction was well-studied. One such reaction previously studied in the condensed phase is that between O(³P) and styrene **3**.^{8,9} Answers to questions about the formation of rearranged styrene byproducts, discussed in this study, have yielded encouraging lessons about the viability of sulfoxides **1,2** to produce O(³P) atoms. Mechanistic information was also provided by adding substituents to the structure of the substrate to vary the electronic and steric effects.

Experimental Section

Chemicals and Instrumentation. Reagents and solvents were obtained commercially [1,2-benzodiphenylene sulfide, dibenzothiophene sulfide, benzene (anhydrous), phenol, biphenyl, diphenyl sulfoxide, acetonitrile (anhydrous), and acetonitrile-*d*₃] and were used as received. Diphenyl sulfide was distilled under reduced pressure (bp 124 °C/6 mmHg). Compounds **1** and **2** were prepared either by using a literature method²³ or by reaction with *m*-chloroperoxybenzoic acid. Samples were stored in the dark at 25 °C and replaced every 3–6 weeks. Gas chromatographic data were acquired 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 a Shimadzu-17A auto-sampler capillary gas chromatograph equipped with a flame ionization detector. Additional measurements were carried out on a Bruker (250 MHz) FT-NMR spectrometer. Photolyses were conducted 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 (linear dispersion equal to ca. ±12 nm).

Data Analysis. Concentrations of 1,2-benzodiphenylene sulfoxide, 1,2-benzodiphenylene sulfide, dibenzothiophene sulfide, dibenzothiophene sulfide, phenylacetaldehyde, acetophenone, benzaldehyde, phenol, di-*tert*-butyl sulfoxide, di-*tert*-butyl sulfide, diisopropyl sulfoxide, diisopropyl sulfide, diethyl sulfoxide, para-substituted styrenes (*p*-X-C₆H₄CH=CH₂), para-substituted styrene oxides, and para-substituted arylsulfoxides (*p*-X-C₆H₄)₂SO, where X = OMe, Me, H, Cl, were detected by reference to calibration curves constructed from authentic samples. Excellent linear correlations were observed in the calibration curves (*r*² ≥ 0.999). The study was conducted at room temperature. Sulfoxide photodeoxygenation reactions were carried out with 1.5-mL airtight GC vials or 5-mm NMR

tubes. Argon was flushed through the reaction mixtures prior to irradiation. The reagents were checked by GC or GCMS to establish that no oxidation products were present before photolysis. A typical experiment was conducted using 385 nm light in anhydrous acetonitrile, which contained 5–10 mM **1**, 0.05 M styrene **3**, and 5 × 10⁻⁴ M biphenyl as an internal standard. The photodeoxygenation studies were conducted in an identical fashion for **2** with the exception of using 350-nm light. Product distributions are the average of 2–4 runs. Both epoxide and rearranged byproducts were monitored. The percent conversion of the reaction components was kept below 10% since some products, in particular (*p*-X-C₆H₄)₂SO, can be further oxidized. Relative rates were determined by competition of substrates with benzene, styrene, and/or diphenyl sulfide, where the appearance of the oxidation products were followed. Under the photolysis conditions there is negligible rearrangement of the product styrene oxide. Control experiments demonstrate that styrene is inert to **1** and **2** in the absence of light. Acetonitrile solvent was chosen because of its low relative reactivity toward O(³P) atoms^{5,24} and for the reason that charge-transfer processes are often investigated in this solvent.²⁵

Theoretical Methods. Density functional theoretical (DFT) and PM3 semiempirical calculations were performed with the Gaussian-94 or Gaussian-98 program packages.^{26,27} Geometries were optimized with the B3LYP method along with the 6-31G(d) basis set, or were optimized with the PM3 method. Polarized continuum model (PCM)^{28,29} and self-consistent reaction field (SCRF) single-point calculations at the B3LYP/6-31(d) level were performed on the B3LYP/6-31G(d) or PM3 derived stationary points to model solvent effects. A dielectric constant of 37.5 was used to simulate the solvent acetonitrile.

Results and Discussion

This study concentrated on two topics regarding the photolysis of **1** and **2**. First, on the results of the oxidation of styrene **3**. Second, on the dependence of substrates that provided an opportunity to vary the electronic and steric effects. The experiments and computations provided evidence for the formation of O(³P) from **1,2**-photodeoxygenation in which a charge-transfer interaction between O(³P) and substrate precedes oxidation.

Oxidation of Styrene. Styrene **3** forms five products from a liquid-phase reaction of O(³P) produced by micro-

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SCHEME 2

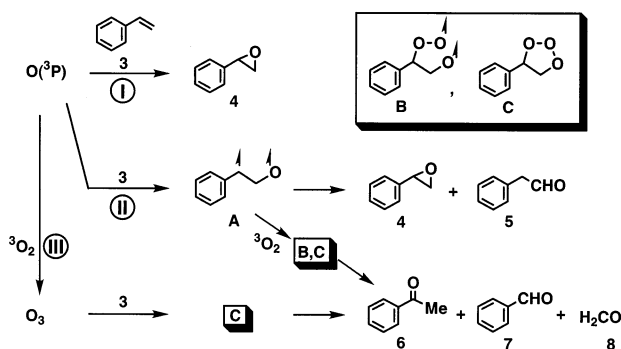


TABLE 1. Comparison of Product Distributions (%) for Styrene Oxidation in Sulfoxide Photodeoxygenation Relative to Microwave Discharge Methods (MDM) that Generate $O(^3P)$ Atoms

entry	cond.	Relative Yields ^{a,b}				ref.
1.	1,2 + hv ^{c,d,e}	58	42	0	0	this work
2.	1,2-O ₂ + hv ^{c,d,f}	47	32	5	16	this work
3.	MDM-N ₂ O/N ₂ (neat) ^g	62	31	2	5	8,9
4.	MDM-O ₂ (decane) ^g	57	27	9	7	8,9
5.	MDM-O ₂ (neat) ^g	44	25	12	19	8,9

^a Relative yields determined by GC or GCMS. ^b Formaldehyde **8** was not detected in the GC and GCMS analyses. ^c Photolysis of **1** (10 mM) was carried out in the presence of 385-nm light in MeCN. Photolysis of **2** (10 mM) was carried out in the presence of 350-nm light in MeCN. Product distributions are averaged since identical results are observed, to within experimental error ($\pm 4\%$), when **1** and **2** are used as the oxygen source. ^d Product distributions are the average of 2–4 runs. ^e Argon was flushed through the reaction mixture for 15–30 min prior to irradiation. ^f Argon was flushed through the reaction mixture for 30 s to 5 min prior to irradiation. ^g The microwave discharge methods generate $O(^3P)$ in the presence of other active oxygen species, such as $O(^1D)$, 1O_2 , 3O_2 , and O_3 .

wave discharge and the difference in regioselectivity is pronounced (**4–8**, Scheme 2).^{8,9} The $O(^3P)$ styrene oxidation pattern is potentially useful since rearrangement effects can be compared with those arising from the active oxygen species produced in the photolysis of **1** and **2**. The results of the photooxidation reaction of **1** or **2** with styrene are shown in Table 1. Styrene partially rearranged during the oxidation. In the presence of 385-nm light and styrene (0.05 M) in argon-saturated acetonitrile at room temperature, **1** (10 mM) deoxygenated to give styrene oxide (**4**), phenylacetaldehyde (**5**), and 1,2-benzodiphenylene sulfide. The chemistry is identical to within experimental error ($\pm 4\%$) when dibenzothiophene sulfoxide **2** is used as the oxygen source along with 350-nm light. The mixture of epoxide **4** to phenylacetaldehyde **5** is 58:42 and the yield is 68% (entry 1, Table 1). In the photodeoxygenation of **1** and **2** the formation of phenylacetaldehyde **5** is competitive with epoxide **4** formation, but not with acetophenone (**6**) nor benzaldehyde (**7**). However, **6** and **7** can be formed when Ar purging of the sample is incomplete and molecular oxygen O_2 remains in solution (entry 2, Table 1). We find that when the acetonitrile medium contains dissolved O_2 , **1** and **2** react photochemically with styrene through a mechanism

involving **6** and **7**. Formaldehyde (**8**) was not detected with our GC and GCMS analyses.

A similar styrene oxidation pattern is observed with the microwave discharge method of generating $O(^3P)$ atoms.^{8,9} The N_2/N_2O discharge reaction of $O(^3P)$ with styrene gave epoxide **4** and phenylacetaldehyde **5** in a 62:31 ratio along with the byproducts acetophenone **6** and benzaldehyde **7** (entry 3, Table 1). The epoxide **4** potentially forms in a concerted or a stepwise process (Scheme 2I,II). The yield of **6** and **7** increased when an O_2 discharge was used, suggesting O_2 contributes to their formation (compare entries 3–5). Acetophenone **6** and benzaldehyde **7** byproducts were suggested to result from a 3-step mechanism involving oxidative attack of $O(^3P)$ with styrene followed by addition of O_2 , to yield **B** or **C** (Scheme 2II).⁸ A dependence on O_2 concentration is consistent with promoting its attack on an initially formed diradical **A**.⁸ In addition, a reaction may proceed where $O(^3P)$ reacts with O_2 at diffusion control⁵ to yield ozone (Scheme 2III),³⁰ then ozonide **C**, and ultimately **6–8**.

A previously studied system provides a possible context for the data in Table 1. Jenks³ and Mazur^{8,9} observed the randomization of epoxide stereochemistry, which suggested a possible stepwise reaction of $O(^3P)$ with the double bond of β -methyl styrene (**9** and **10**, Scheme 3). The photolysis of **2**³ yielded an epoxide ratio similar to that obtained by using microwave discharge (N_2/N_2O)^{8,9} to produce $O(^3P)$ in the condensed phase (Scheme 3A,B). Unfortunately, data are unavailable in the Jenks³ and Mazur studies^{8,9} to compare possible similarities between ketone products resulting from 1,2-H shifts, alcohol products, or products arising from an oxidative cleavage. A resulting triplet diradical intermediate with rotation about the C–C bond was suggested to explain the mixture of cis and trans epoxides observed.^{3,8,9} The isomerization efficiency indicates that ring-closure of the diradical intermediate must be rapid since isomerization is incomplete³ or else there is a competitive reaction with concerted addition of $O(^3P)$ (Scheme 3B).³¹ Ab initio UHF calculations predicted a low ~ 2 kcal/mol barrier to rotation about the C–C bond, where the $^3(\sigma\pi)$ state can undergo surface crossing to the $^1(\sigma\sigma)$ state to ring close to yield the epoxide.^{32,33} Surface-crossing studies have suggested that $O(^1D)$ intercedes on the path to products in the reaction of $O(^3P)$ with cyclohexane clusters in the liquid phase.¹⁰ Complexing reactions of $O(^3P)$ have been reported. A triplet $CHCl_3 \cdots O$ complex has been characterized in the atomic $O(^3P)$ oxidation of chloroform in a matrix infrared study.³⁴

Since the oxidation reactions of **3**, **9**, and **10** are not stereospecific this suggests that radicals or even radical ions may be involved.³⁵ The 1,2-H shift data on phenylacetaldehyde in Table 1 are reminiscent of an electron-transfer reaction observed between high-valent iron

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SCHEME 3

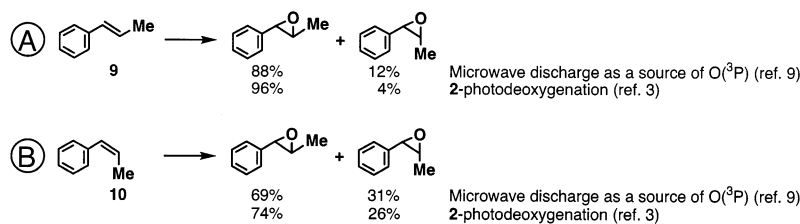


TABLE 2. Relative Rates for $O(^3P)$ or Sulfoxide Photooxygenation of Substrates along with Literature Half-Wave and Ionization Potentials and DFT Computed Ionization Potentials

entry	substrate	$\log k_{rel}$	IP_{expt}^a (eV)	$IP_{gas/DFT}^b$ (eV)	$IP_{MeCN/DFT}^c$ (eV)	$E_{1/2}$ (V) ^d
1.	Cl^-	2.28 ^e (2.3) ^f				
2.	$P(OMe)_3$	2.10 ^e	8.8	9.1	6.7	
3.	cyclopentene	1.73 ^e (1.8) ^g	9.0			
4.	$(p\text{-MeOC}_6\text{H}_4)_2\text{S}$	3.15 ^f	7.79	6.8	4.5	
5.	$(p\text{-MeC}_6\text{H}_4)_2\text{S}$	3.07 ^f	7.83	7.0	5.0	
6.	$(C_6H_5)_2S$	2.62 ^f	8.04	7.3	5.1	
7.	$(p\text{-ClC}_6\text{H}_4)_2\text{S}$	2.44 ^f	8.13	7.4	5.2	
8.	$p\text{-MeOC}_6\text{H}_4\text{CH}=\text{CH}_2$	1.38 ^g	8.15	7.3	5.1	
9.	$p\text{-MeC}_6\text{H}_4\text{CH}=\text{CH}_2$	1.15 ^g	8.38	7.7	5.3	
10.	$C_6H_5\text{CH}=\text{CH}_2$	1.03 ^g	8.9	8.0	5.5	
11.	$p\text{-ClC}_6\text{H}_4\text{CH}=\text{CH}_2$	0.94 ^g	9.1 ⁱ	7.9	5.5	
12.	$t\text{Bu}_2\text{S}$	3.09 ^g	8.13 ^j			1.65
13.	$i\text{Pr}_2\text{S}$	3.41 ^g	8.15 ^j			1.63
14.	$n\text{Bu}_2\text{S}$	3.76 ^g	8.23 ^j			
15.	Et_2S	3.87 ^g	8.45 ^j			1.65
16.	Me_2S	3.61 ^h	8.71 ^j	8.6 ^k	5.6 ^k	
17.	C_6H_6	0	9.9			

^a Experimental adiabatic ionization potentials from ref 52. ^b Geometries optimized with the PM3 semiempirical method followed by a single-point calculation at the B3LYP/6-31G(d) and UB3LYP/6-31G(d) levels. ^c PCM calculations at the B3LYP/6-31G(d) and UB3LYP/6-31G(d) levels from PM3 optimized minima. A dielectric constant of 37.5 is used to simulate acetonitrile. ^d Half-peak potentials vs SCE in acetonitrile (ref 45). ^e Value from the irradiation of pyridine *N*-oxide (ref 5). ^f Value from the irradiation of 1,2-benzodiphenylene sulfoxide **1** (ref 1). ^g This work. Relative rates were determined by competition with benzene, styrene, or diphenyl sulfide in the photolysis of **1**. ^h Value from the gas-phase mercury-sensitized decomposition of N_2O (ref 50). ⁱ IP estimated as 9.1 eV from the IPs of a series of para-substituted diaryl sulfides. ^j IPs estimated from the corresponding oxygenated molecules (refs 52 and 53). ^k Geometry optimized at the B3LYP/6-31G(d) level.

porphyrins and styrene,^{36–38} where styrene rearrangement occurs via a radical cation.³⁹ Resolving questions about the influence of electronics in the sulfoxide photolysis process seemed like an important next step. The influence of solvation diminishes the energy required to form radical cations in styrene and diaryl sulfide trapping agents according to polarized continuum model UB3LYP calculations (Table 2).

Influence of Ring Substituents. We have examined a series of para-substituted styrenes in the photodeoxygenation of **1** and **2**. The experiments provide evidence that sulfoxide photolysis underpins the production of $O(^3P)$, which provides mechanistic insight on the process that gives rise to hydrocarbon oxidation. Competition between substituted styrenes for the oxygenating intermediate produced in the photolysis of **1** and **2** yielded a linear correlation with σ^+ ($r^2=0.996$, Figure 1). The magnitude of the reaction constant, $\rho^+ = -0.48$, is consistent with trapping of an electrophilic oxidant⁴⁰ and suggests a build-up of positive charge on the alkene in the transition state. The excellent correlation of the rate data with σ^+ is less satisfactory against σ_p ($r^2 = 0.926$,

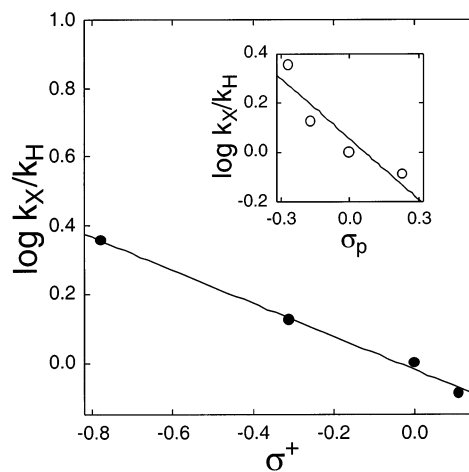


FIGURE 1. Plot for $\log k_X/k_H$ vs the Hammett–Brown σ^+ for para-substituted styrene trapping of an intermediate in the photodeoxygenation of **1** and **2** in acetonitrile [slope (ρ^+) = -0.48 , $r^2 = 0.996$]. Inset: Plot for $\log k_X/k_H$ vs the Hammett σ_p for para-substituted styrene trapping of an intermediate in the photodeoxygenation of **1** and **2** in acetonitrile [slope (ρ) = -0.82 , $r^2 = 0.926$].

Figure 1, Inset). Data sets which correlate with σ^+ but not with σ_p are typically thought to possess an electron-deficient site in the transition state, which is in conjugation with an electron-donating substituent.^{41,42} It is tempting to suggest that through-bond resonance is

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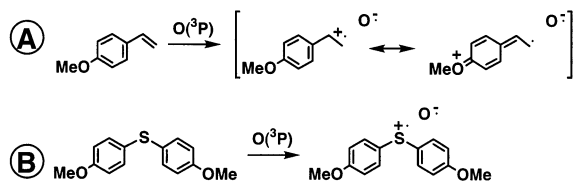
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SCHEME 4



avored in the para-substituted styrenes, where C–C overlap is achieved between the ring and side chain to yield the resonance contributions shown in Scheme 4A.⁴³

A distinction may be made between conjugated and nonconjugated transition states in the substrate due to relative contributions of resonance⁴⁴ by using the rate data of para-substituted styrenes and diaryl sulfides (Table 2). In contrast to the para-substituted styrenes, the para-substituted diaryl sulfides yielded a linear correlation with σ_p values, but was less satisfactory with σ^+ . The correlation coefficient of the Hammett plot of (*p*-X-C₆H₄)₂S determined from the slope of a plot of $\log k_X/k_H$ vs σ_p is enhanced ($r^2 = 0.968$)¹ compared to a plot vs σ^+ ($r^2 = 0.913$). We propose that through-bond resonance is not favored in the substituted diaryl sulfides (Scheme 4B) since, as with RC₂=SR₂ ylides, the C–S overlap is poor. In a similar vein, the behavior of para-substituted diaryl sulfides in the photodeoxygenation of **1** and **2** may be analogous to that of the reaction of ¹O₂ with para-substituted aryl sulfides.⁴⁵ In the *p*-X-C₆H₄SCH₃–¹O₂ study, Foote and Kacher found that a Hammett plot vs σ_p gives an excellent correlation, while use of σ^+ gives a poor correlation.⁴⁵

Little data are available in the literature regarding Hammett ρ values for reactions involving O(³P) atoms.⁴⁶ The Hammett data by itself provides limited evidence for a discrete O(³P) intermediate in the photolysis of **1,2**. It is possible that sulfoxide may act as an oxygen donor in the excited state. In fact, some sulfoxides are known to undergo bimolecular photochemical reductions in the presence of alkoxides in alcoholic solvents.⁴⁷ Our results suggest that electronics of the substrate is in part responsible for the oxygen donor properties of **1** and **2**.

Charge-Transfer Interaction. In the photolysis of **1** and **2**, the interaction of the oxygen intermediate as measured by $k_{(\text{fastest})}/k_{(\text{slowest})}$ is more sensitive to electronic effects for the diaryl sulfides (5.1) compared to the styrenes (2.7) (entries 4–11, Table 2). Even though knowledge is limited on the O(³P) intermediate in solution, one would expect reaction rates to be enhanced with substrates of higher nucleophilicity or reduced ionization potentials (IP) (Table 2). In the past, gas-phase studies of O(³P) have correlated a dependence with IPs of the acceptor molecules.^{1,31,40,46,49,50} Bucher and Scaiano⁵ suggested that O(³P) reactions in acetonitrile solution may yield rates above diffusion-control with the electron-rich substrates bromide ion and chloride ion.

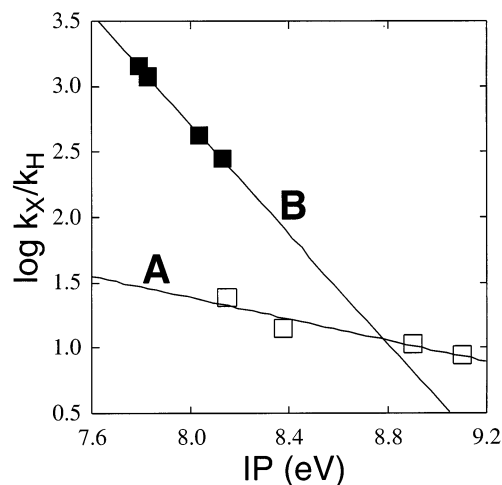


FIGURE 2. Correlation of $\log k_X/k_H$ with the adiabatic ionization potentials for the oxidation of substituted styrene and diaryl sulfide trapping agents. Oxidation of para-substituted styrenes (X = MeO, Me, H, Cl) from the photodeoxygenation of **1** and **2** in acetonitrile (A, open squares, slope = -0.41 , $r^2 = 0.954$). Oxidation of para-substituted diaryl sulfides (X = MeO, Me, H, Cl) from the photodeoxygenation of **1** and **2** in acetonitrile (B, solid squares, slope = -2.10 , $r^2 = 0.999$). Each point represents the average of the product distribution from four runs. Two of the runs contained **1** as the oxygen source, the other two contained **2**. The experimental error is $\pm 4\%$.

The oxygen donor properties are similar in the sulfoxide **1,2**-photodeoxygenation^{1–3} and in the pyridine *N*-oxide photodeoxygenation.⁵ We have explored reactions of tetrabutylammonium chloride¹ and cyclopentene in the photolysis of **1** and **2**. The results suggest a remarkably similar behavior between our product-based and Scaiano's kinetic-based selectivities⁵ for chloride ion and cyclopentene (compare entries 1 and 3, Table 2). However, this close agreement may be partly fortuitous upon scrutinizing the data collected for diphenyl sulfide. The k_{rel} value for diphenyl sulfide was obtained in benzene. The concentrations were chosen to reduce the possibility for sulfoxides to form dimeric structures in a bimolecular reaction (5–10 mM). The k_{rel} value was obtained from observing a small relative concentration of phenol compared to a high concentration of Ph₂SO, which gave a precision of only $\pm 25\%$. In contrast, the k_X/k_H value determined within the Hammett series (*p*-X-C₆H₄)₂S had a precision of $\pm 4\%$. The same situation applied with styrene. Precision was low on competition of benzene with styrene, but high with competition between pairs of the Hammett series, *p*-X-C₆H₄CH=CH₂.

How efficient a charge-transfer or an electron-transfer process will be in the oxygenation process may be inferred from the observed slopes of $\log k$ vs IP for the para-substituted styrenes and para-substituted diaryl sulfides (Figure 2). Here we used an analysis similar to that of Perrin and co-workers.³⁵ If a full electron is transferred at the transition state, and if the energy level of that electron is raised by 1 eV (23 kcal/mol), then the rate constant would be expected to increase by a factor of $\exp(23/RT)$, or 1.6×10^{17} at 20 °C.³⁵ Figure 2 shows that a plot of $\log k$ vs IP is linear with a slope that is dependent on the IP of the substrate. The sensitivity of the slope with IP of the substrate is consistent with an electron transfer at the transition state, only to the extent of 2%

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for para-substituted styrene (Figure 2A) and 12% for para-substituted diaryl sulfide (Figure 2B). The slope for k_x/k_H is more than 5 times larger for diaryl sulfide than styrene. This is consistent with the idea that $O(^3P)$ acts between nonconjugated and conjugated transition states in the substrate due to relative contributions of resonance (Scheme 4). One might suggest that electron donation enhances the formation of product due to a developing charge in $p\text{-MeO-C}_6\text{H}_4\text{CH=CH}_2^{\delta+}\text{-O}^{\delta-}$ and $(p\text{-MeO-C}_6\text{H}_4)_2\text{S}^{\delta+}\text{-O}^{\delta-}$, where solvation in acetonitrile is increased compared to less polar reagents and products. The data are consistent with a charge-transfer dependence of the active oxygen species and the electron density on the alkene and sulfide trapping agent.

Influence of Sterics vs Electronics. The substrates in Table 2 provide the first opportunity to compare the steric and electronic effects in the photodeoxygenation of **1** and **2**. How the substrate structure effects the intermediate along the sulfoxide photoreduction pathway was sought. The interaction of the oxygen intermediate with substrate as measured by k/k_0 appears to be more sensitive to electronic effects than to steric effects. The reduced importance of steric interactions in substituted alkyl sulfides (entries 12–16) is shown by the observation of a poor linear correlation in a Taft plot when $\log(k^R/k^{Me})$ is plotted versus E_s ($\delta = 0.435$; $r^2 = 0.871$). Steric effects appear to play a minor role in determining the outcome of the reaction. The alkyl sulfides, diethyl sulfide, diisopropyl sulfide, and di-*tert*-butyl sulfide, possess nearly identical oxidation potentials [$E_{1/2}$ (V)], and yet the decrease in rate is less than 4-fold (Table 2). This compares to the approximate 110-fold decrease in rate in the same series for 1O_2 .⁴⁵ Steric interactions are known to decrease the yield of alkyl sulfides with 1O_2 ⁴⁵ by affecting physical quenching and chemical reaction pathways. However, only the latter pathway would be available in a mechanism involving the ground-state agent $O(^3P)$. The relative rates for $t\text{Bu}_2\text{S}$ and $i\text{Pr}_2\text{S}$ were determined by monitoring the loss of starting material (entries 12 and 13, Table 2) given the fact branched alkyl sulfides have a potential to oxidatively cleave.⁴⁸ In doing so, enhanced experimental errors ($\pm 20\%$) were observed for these measurements.

The indirect trapping data are rationalized by suggesting that it is the electron-donating ability of the substrates and not the steric interaction with the approaching oxidant that dictates the magnitude of k . Atomic $O(^3P)$ is a reasonable candidate for the electrophilic species trapped in the Hammett, IP, and Taft studies. Laser studies involving atomic oxygen $O(^3P)$ have also recorded a dependence on the ionization potential of the substrate.⁵¹

Conclusion

We have studied the mechanism of sulfoxide photochemistry and provide evidence for the oxygenation of saturated¹ and unsaturated hydrocarbons. A liquid-phase

photolysis of **1** and **2** was used to generate atomic oxygen [$O(^3P)$] or an equivalent active oxygen species capable of oxygen transfer to the hydrocarbons. Our study focused on the results of oxidation products in the reaction of styrene **3** and on substrates that provided an opportunity to vary the electronic and steric effects. The reaction was similar to sulfoxide photodeoxygenation in a microwave discharge method for generating $O(^3P)$ atoms.⁹ Sulfoxide photodeoxygenation is a potentially clean method for $O(^3P)$ production compared to the microwave discharge method.^{8,9} With Argon purging of the sulfoxide sample before photolysis, the method can preclude a secondary oxidation process involving molecular oxygen. Microwave discharge methods produce $O(^3P)$, but do so typically in the presence of O_2 , which can lead to the production of singlet molecular oxygen and ozone along with ozonides and carbonyl oxides in reactions with alkenes.^{8,9}

The findings from this study may establish a way to generate high-value oxygenated compounds from readily available petroleum molecules. Functionalization of hydrocarbons takes place under mild photolysis conditions of **1** and **2**, which leads to a possibility for the synthetic use of atomic oxygen, $O(^3P)$. Electrophilic triplet oxygen atoms react mainly at tertiary C–H bonds of alkanes, based on relative bond strengths, $3^\circ < 2^\circ < 1^\circ$, to give the corresponding alcohol molecules.^{1–4} Functionalization of alkenes, such as styrene **3**, gives rise to epoxide and ketone products where a preference exists for oxygenation of the side chain rather than the ring of styrene. It may be noted that hydroxyl radicals are more reactive and less selective toward hydrocarbons compared to $O(^3P)$ atoms.⁵ Oxygen (3P) atoms balance reactivity and selectivity and involve the oxidation of inert alkanes typically inaccessible to the oxidants peracid, dioxirane, ozone, and singlet molecular oxygen. The sulfoxide system provides support for the application of this photooxygenation procedure in other substrates. Future research will be based on the idea that a catalyst present at the outset may aid in the transfer of oxygen from sulfoxide to a hydrocarbon. Polyoxomolybdates⁵⁴ and polyoxotungstates^{55,56} have been studied in a similar manner for catalysis under photochemical conditions.

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, with start-up funds from the City University of New York, and by a research award from PSC-CUNY. We thank Professors Charlie Perrin and Spiro Alexandratos for stimulating discussions and Chengguo Dong for work on *p*-chlorostyrene in an early phase of the project.

Supporting Information Available: Descriptions of the computed geometries of all stationary points (Cartesian coordinates) and absolute energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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