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

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

We sought to establish the mechanistic criteria to learn of a possible sulfoxide method to generate O(P) atoms or an equivalent active oxygen species. Microwave discharge methods generate O(P), but often in the presence of other reactive species, such as O(1D), O\textsubscript{2}, and O\textsubscript{3}.\textsuperscript{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(P) and styrene.\textsuperscript{3,8} Answers to questions about the formation of rearranged styrene byproducts, discussed in this study, have yielded encouraging lessons about the viability of sulfoxides, which are often 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\textsuperscript{-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-C\textsubscript{6}H\textsubscript{4})\textsubscript{2}SO, can be further oxidized. Relative rates were determined by competition of substrates with benzene, styrene, and/or diethyl 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(P) atoms\textsuperscript{23,24} and for the reason that charge-transfer processes are often investigated in this solvent.\textsuperscript{25}

Theoretical Methods. Density functional theoretical (DFT) and PM3 semiempirical calculations were performed with the Gaussian-94 or Gaussian-98 program packages.\textsuperscript{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)\textsuperscript{28,29} and self-consistent reaction field (SCRF) single-point calculations at the B3LYP/6-31G(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.\textsuperscript{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(P) from 1,2-photodeoxygenation in which a charge-transfer interaction between O(P) and substrate precedes oxidation.

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

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wave discharge and the difference in regioselectivity is pronounced (4–8, Scheme 2). 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 photodeoxygenation 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 medium contains dissolved O2, 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. The N2/N2O 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 21). The yield of 6 and 7 increased when an O2 discharge was used, suggesting O2 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 O2, to yield B or C (Scheme 2II). A dependence on O2 concentration is consistent with promoting its attack on an initially formed diradical A. In addition, a reaction may proceed where O(3P) reacts with O2 at diffusion control to yield ozone (Scheme 2III), then ozonide C, and ultimately 6–8.

A previously studied system provides a possible context for the data in Table 1. Jenks and Mazur observed the randomization of epoxide stereochemistry, which suggested a possible stepwise reaction of O(3P) with the double bond (β-methyl styrene) (9 and 10, Scheme 3). The photolysis of 21 yielded an epoxide ratio similar to that obtained by using microwave discharge (N2/N2O) to produce O(3P) in the condensed phase (Scheme 3A, B). Unfortunately, data are unavailable in the Jenks and Mazur studies 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. The isomerization efficiency indicates that ring-closure of the diradical intermediate must be rapid since isomerization is incomplete or else there is a competitive reaction with concerted addition of O(3P) (Scheme 3B). Ab initio UHF calculations predicted a low ~2 kcal/mol barrier to rotation about the C–C bond, where the 3(ax) state can undergo surface crossing to the 1(aw) state to ring close to yield the epoxide. 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. Complexing reactions of O(3P) have been reported. A triplet CHCl3–O complex has been characterized in the atomic O(3P) oxidation of chloroform in a matrix infrared study.

Since the oxidation reactions of 3, 9, and 10 are not stereospecific this suggests that radicals or even radical ions may be involved. The 1,2-H shift data on phenylacetaldehyde in Table 1 are reminiscent of an electron-transfer reaction observed between high-valent iron...
The excellent correlation of the rate suggests a build-up of positive charge on the alkene in consistent with trapping of an electrophilic oxidant and generation of 2-photodeoxygenation (ref. 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

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>log k_{rel}</th>
<th>IP_{expt} (eV)</th>
<th>IP_{MeCN/DFT} (eV)</th>
<th>IP_{MeCN/DFT} (eV)</th>
<th>E_{1/2} (V)</th>
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<tr>
<td>1</td>
<td>Cl^-</td>
<td>2.28 (2.3)</td>
<td>9.1</td>
<td>6.7</td>
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<tr>
<td>2</td>
<td>P(OMe)_2</td>
<td>2.10</td>
<td>8.8</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>cyclopentene</td>
<td>1.75 (1.8)</td>
<td>9.0</td>
<td>5.1</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td>(p-MeOCH_2)S</td>
<td>3.15</td>
<td>7.9</td>
<td>4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(p-MeC_6H_4)S</td>
<td>3.07</td>
<td>7.8</td>
<td>5.0</td>
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<td></td>
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<tr>
<td>6</td>
<td>(C_6H_5)S</td>
<td>2.62</td>
<td>8.0</td>
<td>5.1</td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>(p-CIC_6H_4)S</td>
<td>2.44</td>
<td>8.1</td>
<td>5.2</td>
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<td></td>
</tr>
<tr>
<td>8</td>
<td>p-MeOCH_2CH=CH_2</td>
<td>1.39</td>
<td>8.1</td>
<td>5.1</td>
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<tr>
<td>9</td>
<td>p-MeC_6H_5CH=CH_2</td>
<td>1.15</td>
<td>8.3</td>
<td>5.3</td>
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<tr>
<td>10</td>
<td>C_6H_5CH=CH_2</td>
<td>1.03</td>
<td>8.9</td>
<td>5.5</td>
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<tr>
<td>11</td>
<td>p-CIC_6H_5CH=CH_2</td>
<td>0.94</td>
<td>9.1</td>
<td>5.5</td>
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<td>12</td>
<td>tBuS</td>
<td>3.09</td>
<td>8.1</td>
<td>5.5</td>
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<tr>
<td>13</td>
<td>iPrS</td>
<td>3.41</td>
<td>8.15</td>
<td>5.6</td>
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<tr>
<td>14</td>
<td>nBuS</td>
<td>3.76</td>
<td>8.23</td>
<td>5.6</td>
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<tr>
<td>15</td>
<td>EtS</td>
<td>3.87</td>
<td>8.45</td>
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<td>16</td>
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<td>3.61</td>
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<td>17</td>
<td>C_6H_6</td>
<td>0</td>
<td>9.9</td>
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</table>

*Experimental adiabatic ionization potentials from ref 52. *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. *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. *Value from the irradiation of 1,2-benzodiphenylene sulfoxide (ref 1). *Value from the gas-phase mercury-sensitized decomposition of N_2O (ref 50). *1P estimated as 9.1 eV from the IPs of a series of para-substituted diaryl sulfides. *IPs estimated from the corresponding oxygenated molecules (refs 52 and 53). *Geometry optimized at the B3LYP/6-31G(d) level.

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 ρ + (r^2 = 0.996, Figure 1). The magnitude of the reaction constant, ρ + = -0.48, is consistent with trapping of an electrophilic oxidant(39) and suggests a build-up of positive charge on the alkene in the transition state. The excellent correlation of the rate data with ρ + is less satisfactory against α_p (r^2 = 0.926, 0.82, 0.926).

Figure 1, Inset). Data sets which correlate with ρ + but not with α_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 tempting to suggest that through-bond resonance is not with the participating π system. The experiments provide evidence that styrene rearranges to 2-photodeoxygenation (ref. 3). Page 38 where styrene rearranges...
favored 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 \( \alpha_p \) values, but was less satisfactory with \( \alpha_s \). The correlation coefficient of the Hammett plot of (p-X-C6H4)2S determined from the slope of a plot of \( \log k_{pH} \) vs \( \alpha_p \) is enhanced \( (r^2 = 0.968) \) compared to a plot vs \( \alpha_s \) \( (r^2 = 0.913) \). We propose that through-bond resonance of the substrate is in part due to the para-substituted diaryl sulfides (Scheme 4B) since, with both \( X = S \) and \( X = S \), 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 \( O_2 \) with para-substituted aryl sulfides.45

In the p-X-C6H5SCH3+O2 study, Foote and Kacher found that a Hammett plot vs \( \alpha_p \) gives an excellent correlation, while use of \( \alpha_s \) gives a poor correlation.45

Little data are available in the literature regarding Hammett \( \rho \) values for reactions involving O(3P) atoms.46 The Hammett data by itself provides limited evidence for a discrete O(P) 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 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 \( k_{\text{forward}}/k_{\text{backward}} \) 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(P) 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 (p-X-C6H4)2S have correlated a dependence with IPs of the acceptor molecules.1,31,40,46,49,50 Bucher and Scaino2 suggested that O(IP) reactions in acetonitrile solution may yield rates above diffusion-control with the electron-rich substrates bromide ion and chloride ion.

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**Figure 2.** Correlation of \( \log k_{pH} \) with the adiabatic ionization potentials for the oxidation of substituted styrene and diaryl sulfide trapping agents. Oxidation of para-substituted styrenes \( (X = \text{MeO, Me, H, Cl}) \) 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 \( (X = \text{MeO, Me, H, Cl}) \) 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-photodeoxygenation1–3 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 Scaino’s kinetic-based selectivities 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 \( k_{\text{rel}} \) 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 \( k_{\text{rel}} \) 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 \( k_{pH} \) 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-C6H4CH2=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 \( 1.6 \times 10^{17} \) 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%
for para-substituted styrene (Figure 2A) and 12% for para-substituted diaryl sulfide (Figure 2B). The slope for \( k_d/k_c \) is more than 5 times larger for diaryl sulfide than styrene. This is consistent with the idea that O(1P) 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-MeO-C\(_2\)H\(_4\)-CH\(_2\)-CH\(_2\)-S\(_2\)C\(_6\)H\(_4\) and p-MeO-C\(_2\)H\(_4\)-CH\(_2\)-CH\(_2\)-S\(_2\)C\(_6\)H\(_4\); 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 \( k_d/k_c \) 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 \( \log(k_d/k_c) \) is plotted versus \( E_p (\Delta = 0.435; r^2 = 0.871) \). Steric effects appear to play a minor role in determining the outcome of the reaction. The alkyl sulfides, diethyl sulfide, disopropyl 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 \( ^1\text{O}_2 \).\(^{45} \) Steric interactions are known to decrease the yield of alkyl sulfides with \( ^1\text{O}_2 \).\(^{46} \) 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(1P). The relative rates for tBu\(_2\)S and iPr\(_2\)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 (±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 \( k_d/k_c \). Atomic O(1P) is a reasonable candidate for the electrophilic species trapped in the Hammett, IP, and Taft studies. Laser studies involving atomic oxygen O(1P) 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 saturated and unsaturated hydrocarbons. A liquid-phase photolysis of 1 and 2 was used to generate atomic oxygen [O(1P)] 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(1P) atoms.\(^{5} \) Sulfoxide photodeoxygenation is a potentially clean method for O(1P) 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(1P), but do so typically in the presence of O\(_2\), which can lead to the production of singlet molecular oxygen and ozone along with oxonides and carbonyl oxides in reactions with alkenes.\(^{5} \)

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(1P). Electrophilic triplet oxygen atoms react mainly at tertiary C–H bonds of alkanes, based on relative bond strengths, \( 3° \prec 2° \prec 1° \), 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(1P) atoms.\(^{5} \) Oxygen (1P) 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 photoxygenation 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. Polyoxomolybdates\(^{54} \) and polyoxotungstates\(^{55,56} \) have been studied in a similar manner for catalysis under photochemical conditions.

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**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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