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# Photooxidations of Sulfenic Acid Derivatives. 5. The Reaction of Singlet Oxygen with Ethyl Phenyl Sulfenate[1]

Edward L. Clennan* and Ming-Fang Chen

*Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070*

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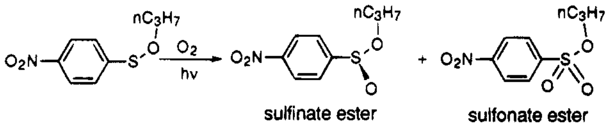
The reaction of ethyl phenylsulfenate ester with singlet oxygen was investigated. The total rate of disappearance of singlet oxygen induced by the sulfenate ester, $k_T$, was measured by monitoring the quenching of the emission of singlet oxygen at 1270 nm. This result coupled with a measurement of the rate of product formation reveals that ethyl phenylsulfenate ester does not physically quench singlet oxygen. Quantitative trapping studies with $Ph_2S$ and $Ph_2SO$ suggest that only one intermediate is kinetically required on the reaction surface. This is in dramatic contrast to sulfides and sulfenamides which require two intermediates. The implications of these results are discussed.

In 1993, Pasto and co-workers[2] reported that 4-nitrobenzenesulfenate esters were converted to 4-nitrobenzenesulfinate esters upon irradiation at 350 nm under an oxygen atmosphere (eq 1). The reactions were quenched by the additions of either 1,3-cyclohexadiene or *trans*-piperylene, and an endoperoxide was isolated from reaction mixtures containing 1,3-cyclohexadiene suggesting that the sulfenate esters act as triplet sensitizers for singlet oxygen formation.



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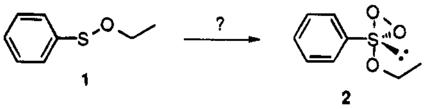
Pasto and Cottard[3] have suggested a mechanism for these reactions, by analogy to published work on sulfide photooxidations, which invoked formations of both persulfoxide and thiadioxirane intermediates. Unfortunately, a detailed mechanistic study of these reactions to verify this proposal is complicated and essentially precluded by the facts that (1) S−O homolytic cleavages occur concurrently with the photooxidations and (2) the 4-nitrophenyl group electronically reduces the reactivity of the sulfenate esters to such an extent that the rate of reaction is inconveniently slow to measure by well-established methods.[4,5] In order to circumvent these problems we have conducted a detailed kinetic study of the photooxidation of the more reactive substrate, ethyl phenylsulfenate, **1**, using an external singlet oxygen sensitizer. These results demonstrate that in contrast to the reactions of singlet oxygen with sulfides or sulfenamides[1] only a single intermediate is kinetically required on the reaction surface for the photooxidation of **1**.



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The current controversy[1] surrounding the proper description of the dialkyl sulfide photooxidation reaction surface and the conspicuous paucity of detailed kinetic studies for reactions at sulfenyl sulfur provides the impetus for this report. Studies of the photooxidations of sulfenate esters in particular are relevant since much of the current debate centers on the question of the structural integrity and viability of thiadioxirane, **2**, intermediates in these reactions. The oxygen atom in a sulfenate ester is anticipated to lend thermodynamic stability to the thiadioxirane by the well-known apical ligand effect in trigonal bipyramidal environments.[6]

## Results and Discussion

The photooxidations of **1** ($6.3 \times 10^{-2}$ M) were conducted at room temperature in oxygen-saturated benzene or $CDCl_3$ solutions containing $5 \times 10^{-5}$ M TPP as a sensitizer. The samples were irradiated with either a 400 W medium-pressure Hanovia or a 750 W tungsten−halogen lamp modified by a 12 M sodium nitrite filter solution. At low conversions (<10%) the sulfinate ester, **1SO**, was the exclusive product of the reaction (Figure 1). The sulfonate ester, **1SO$_2$**, was only observed at higher conversions consistent with its formation by the scavenging of an intermediate with adventitious sulfinate ester produced in the reaction. This speculation is also supported by previously published oxygen labeling results which demonstrated that the two oxygen atoms in **1SO$_2$** originated from different oxygen molecules.[7]

The lifetimes of singlet oxygen, ($\tau = [k_T[\mathbf{1}] + k_d]^{-1}$) in the presence of different concentrations of **1** were measured in benzene by monitoring the decay of singlet oxygen emission at 1270 nm.[4,5] A plot of $1/\tau$ versus [**1**] gave a slope, $k_T$, of $5.58 \times 10^5$ M$^{-1}$ s$^{-1}$.[8] This rate constant is smaller than those reported for diethyl sulfide ($1.71 \times 10^7$ M$^{-1}$ s$^{-1}$)[1] and 4-morpholinyl benzyl sulfide ($1.28 \times 10^6$ M$^{-1}$ s$^{-1}$)[1] as anticipated based upon the electronegativity of the substituents attached to sulfur and on the well-known electrophilicity of singlet oxygen.[9]

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1995.

[1] Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218−4227.

[2] Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *58*, 4110−4112.

[3] Pasto, D. J.; Cottard, F. *J. Am. Chem. Soc.* **1994**, *116*, 8973−8977.

[4] Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581−3584.

[5] Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080−5085.

[6] Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, The Netherlands, 1985; Vol. 19; pp 408−483.

[7] Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952−7954.

[8] This rate constant was collected over a wider range of $\tau$ values and is more accurate than the previously reported rate[1] of $3.46 \times 10^5$M$^{-1}$ s$^{-1}$.

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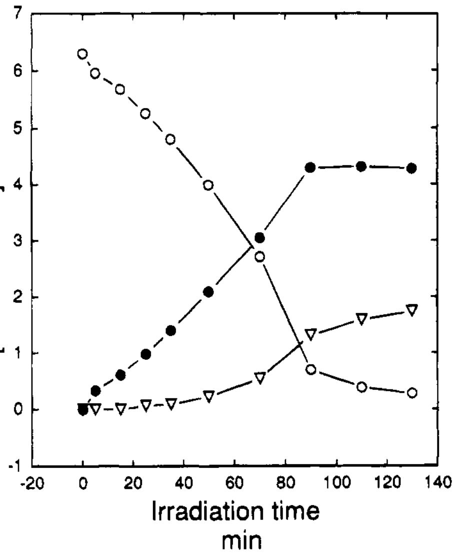


**Figure 1.** Reaction profile for the photooxidation of **1**: ○, **1**; ●, **1SO**; ▽, **$1SO_2$**.

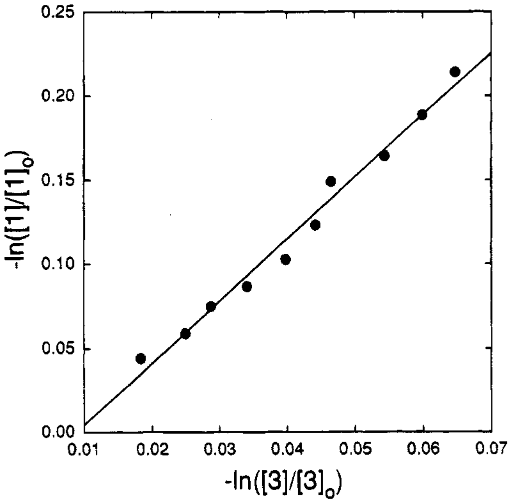


**Figure 2.** Relative rates of product formation plotted according to eq 2: slope = 3.69; intercept = +0.03; $r$ = 0.9914.

The relative rate constant of chemical removal of singlet oxygen from solution by **1** and adamantane adamantylidene, **3**, was measured by the competitive kinetic method of Higgins, Foote, and Cheng.[10] Since problems were encountered with **1** interacting with an intermediate formed in the reaction of **3** (vide infra) the oxidations of the these competing substrates were conducted side-by-side on a merry-go-round to ensure identical steady state singlet oxygen production. In addition, the concentrations of the competing substrates were adjusted to guarantee complete capture of singlet oxygen in both reaction vessels (i.e., $k_T$[substrate] $\gg k_d$). Aliquots were removed at identical time intervals from the two competing reaction mixtures. The concentrations of the reaction components were determined by capillary GC analyses and plotted according to eq 2 (Figure 2). The $k_r$ for **1** ($1.27 \pm 0.02 \times 10^6$ M$^{-1}$ s$^{-1}$) was determined by multiplying the slope of this plot by the $k_r$ for **3** ($3.49 \times 10^5$ M$^{-1}$ s$^{-1}$).[1]

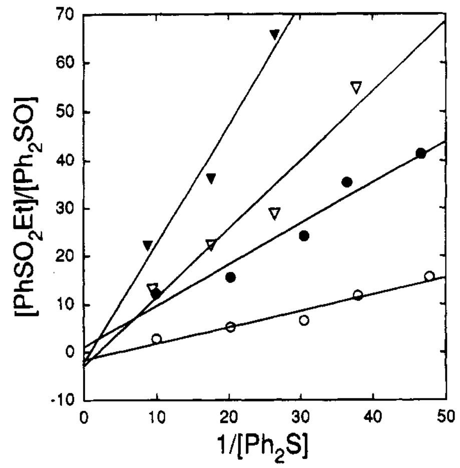
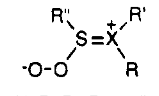


**Figure 3.** Photooxidations of **1** in the presence of $Ph_2S$ plotted according to eq 3: ○, [PhSOEt] = 0.023M, slope = 0.34, $r$ = 0.9684; ●, [PhSOEt] = 0.056 M, slope = 0.86, $r$ = 0.9729; ▽, [PhSOEt] = 0.103 M, slope 1.43, $r$ = 0.9698; ▼, [PhSOEt] = 0.166 M, slope = 2.47, $r$ = 0.9794.

$$\ln\frac{[1]}{[1]_0} = \frac{k_r(1)}{k_r(3)}\ln\frac{[3]}{[3]_0} \tag{2}$$

The relationship between $k_T$, $k_r$, and $k_q$ (rate constant for physical quenching) is given by $k_T = 0.5k_r + k_q$ since two molecules of sulfinate ester are produced for each molecule of singlet oxygen that disappears during the very early stages of the reaction. Therefore, $k_q$ for **1** is too small to measure and the physical quenching of singlet oxygen by **1** does not occur. This behavior is very similar to that observed for sulfenamides[1] but very different from that observed with $Et_2S$ where greater than 95% of the interaction with singlet oxygen is via the physical quenching channel. We previously attributed the lack of physical quenching by sulfenamides to the contribution of resonance structure **4a** to the persulfinamide intermediate which leads to a stronger S−O bond with enhanced s character. A similar factor can also be operating to stabilize the persulfinate intermediate, **4b**. However, removal of the persulfinate ester by a competitive process (vide infra) not available during the photooxidation of either the sulfenamides or sulfides could also contribute to the suppression of physical quenching.



**4a** X = N; R, R', R'' = alkyl or aryl
**4b** X = O; R, R'' = alkyl or aryl; R' = lone pair

Cophotooxidations of **1** with $Ph_2S$ and $Ph_2SO$ resulted in formation of **1SO** and $Ph_2SO$ and $Ph_2SO_2$, respectively. Control reactions demonstrated that both $Ph_2S$ and $Ph_2SO$ are unreactive in the absence of **1**. A quantitative examination of the cophotooxidations demonstrated that plots of [**1SO** ]/[$Ph_2SO_{x+1}$] versus 1/[$Ph_2SO_x$], where $x$ = 0 for $Ph_2S$ and $x$ = 1 for $Ph_2SO$ trapping, are linear with slopes directly proportional to the concentration of **1** (Figures 3 and 4). These results suggest that **1**, $Ph_2S$, and $Ph_2SO$ are all competing for the same intermediate as shown by Scheme 1 and described by eq 3. The rate constant ratio, $k_{rel}$, in eq 3 is $k_1/k_S$ (7.4) and $k_1/k_{SO}$ (0.33) for $Ph_2S$ and $Ph_2SO$ trapping, respectively, and can be determined by plotting the slopes of the lines in Figures

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(9) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765−769.

(10) Higgins, R.; Foote, C. S.; Cheng, H. In *Advances in Chemistry Series*; Gould, R. F. Ed.; American Chemical Society: Washington, D.C., 1968; Vol. 77; pp 102−117.

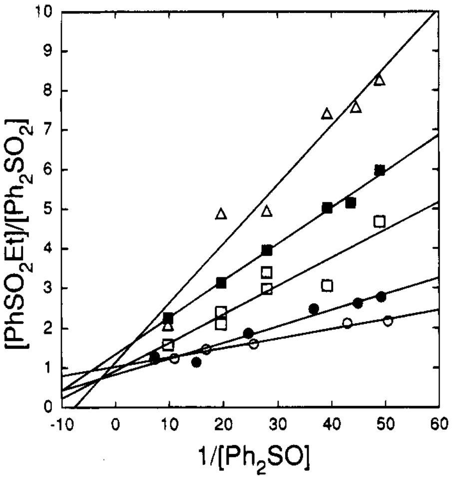
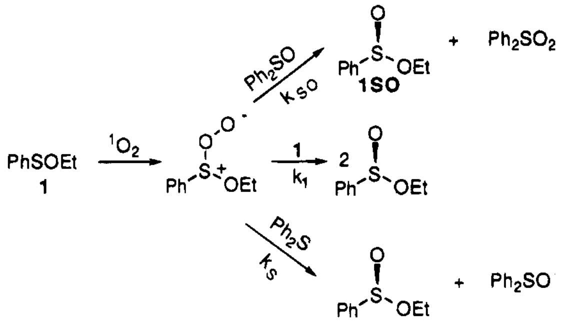


**Figure 4.** Photooxidations of **1** in the presence of Ph$_2$SO plotted according to eq 3: ○, [PhSOEt] = 0.023 M, slope = 0.024, $r$ = 0.99243; ●, [PhSOEt] = 0.056 M, slope = 0.040, $r$ = 0.9704; □, [PhSOEt] = 0.10 M, slope = 0.071, $r$ = 0.9316; ■, [PhSOEt] = 0.16 M, slope = 0.092, $r$ = 0.9966; △, [PhSOEt] = 0.21 M, slope = 0.149, $r$ = 0.9753.

**Scheme 1**

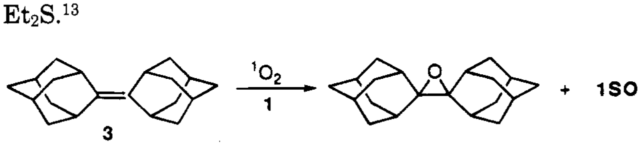


3 and 4 versus the concentrations of **1** used in the experiment. The results demonstrate that Ph$_2$SO is 3

$$\frac{[\mathrm{PhSO_2Et}]}{[\mathrm{Ph_2SO}_{x+1}]} = 1 + \frac{2k_{\mathrm{rel}}[\mathbf{1}]}{[\mathrm{Ph_2SO}_x]} \qquad (3)$$

times better than **1** and 22 times better than Ph$_2$S as a trapping agent for the persulfinate intermediate.

Corroborating evidence that **1** can remove an oxygen atom from a persulfinate intermediate was obtained during an examination of the photooxidations of mixtures of **1** and **3** where it was observed that **1** promoted the formation of adamantane adamantylidene epoxide.[11] Phosphites, (RO)$_3$P, have also been reported to trap intermediates during the photooxidations of **3**[12] and Et$_2$S.[13]



Hammett substituent studies with substituted diaryl sulfides and sulfoxides gave reaction constants, ρ, of 0.34 ($r$ = 0.8833) and 1.41 ($r$ = 0.9818), respectively, indicative of the nucleophilic character of the trapped intermediate (Figure 5). The correlation coefficients provide evidence of the lower quality of the Ar$_2$S in comparison to the Ar$_2$SO plot and reflect the marginal reactivities of the diaryl sulfides (vide supra). As a result, Ar$_2$SO$_2$ as well as Ar$_2$SO were formed in the sulfide Hammett studies even at low conversions (<5%). A linear Hammett plot could only be obtained in this case by recognizing that the amount of sulfide that reacted was equal to the sum of the sulfoxide and sulfone.

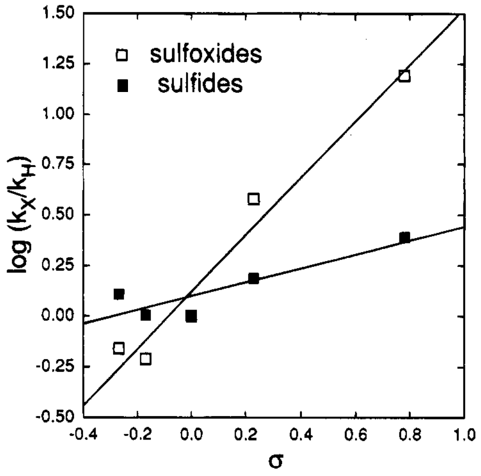


**Figure 5.** Sulfide and sulfoxide Hammett plots.

The mechanism of the very slow oxygen transfer to the diarylsulfides is not known. However, nucleophilic oxidations of sulfides[14] are unknown, and this reaction might be better classified as a biphilic insertion[15] into the O−O bond followed by collapse to two sulfoxides. The reactions of sulfides with peroxides have been reported[16] and in some cases lead to insertion and the formation of sulfuranes.[17] Biphilic insertions have been examined in detail for trivalent phosphorus compounds[18] and are often characterized by very small Hammett reaction constants.[19] These very small reaction constants reflect the fact that the heteroatom is at the same time acting both as an electron donor and acceptor.

## Conclusions

The most economical mechanism for the photooxidation of **1** which provides an explanation for all the experimental data is depicted in Scheme 1. The photooxidation of **1**, therefore represents the first sulfenic acid derivative for which only one reactive intermediate is kinetically required. All of the $^1O_2$ removed from solution by **1** is incorporated into the products, and consequently physical quenching does not occur. In contrast, only 5% of the $^1O_2$ removed from solution by Et$_2$S can be accounted for by product formation.[20] The absence of physical quenching and of a second intermediate in the reaction of **1** can be attributed to either (1) enhanced stability of the

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[11] Clennan, E. L.; Chen, M.-F. Unpublished results.

[12] Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1991**, *32*, 863−866.

[13] Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909−1910.

[14] Oae, S.; Doi, J. T. *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press: Boca Raton, FL, 1991; p 433.

[15] Clennan, E. L.; Heah, P. C. *J. Org. Chem.* **1981**, *46*, 4105−4107.

[16] Wasserman, H. H.; Saito, I. *J. Am. Chem. Soc.* **1975**, *97*, 905−906.

[17] Campbell, B. S.; Denney, D. B.; Denney, D. Z.; Shih, L. *J. Am. Chem. Soc.* **1975**, *97*, 3850−3851.

[18] Bartlett, P. D.; Baumstark, A. L.; Landis, M. E.; Lerman, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 5267−5268.

[19] Clennan, E. L.; Heah, P. C. *J. Org. Chem.* **1984**, *49*, 2284−2286.

[20] Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717−4721.

persulfinate intermediate possibly due to the contribution of resonance structure **4b** or (2) reaction of this intermediate with **1** leading to competitive inhibition of both physical quenching and the interconversion to a second intermediate.

## Experimental Section

**General Aspects.** Proton and carbon NMR were obtained either on a JEOL GX 270 or 400 MHz NMR and are referenced internally to TMS. The GC/MS were collected on a Hewlett-Packard instrument consisting of a 5890 series II GC and a 5971 series mass selective detector. All reactions were analyzed on a Perkin-Elmer Autosystem capillary gas chromatograph equipped with a HP-5 30 m × 0.25 mm × 0.25 $\mu$m (length × inside diameter × film thickness) capillary column. **1** was synthesized using the method of Moore and O'Connor.[21] Ethyl benzenesulfinate, **1SO**, and ethyl benzene sulfonate, **1SO$_2$**, were identified by $^1$H NMR and GC/MS and by comparison to literature reports.[22] TPP, adamantanone (99%), and thiophenol were all obtained from Aldrich and used without further purification. Biphenyl was recrystallized from hexane–ethyl acetate (100:1) and its purity checked by GC prior to use. Diphenyl sulfide (Aldrich 98%) was distilled under reduced pressure (bp 124 °C/6 mmHg). $Ph_2SO$ was recrystallized from hexane–methylene chloride or hexane–ethyl acetate and its purity checked by GC prior to use. Benzene was refluxed over $P_2O_5$ for 5 h and then distilled under a nitrogen or argon atmosphere.

**Hammett Studies.** The Hammett studies were conducted with solutions containing $1.05 \times 10^{-3}$ M biphenyl as an internal standard and $4 \times 10^{-5}$ M TPP as the sensitizer. The concentrations of the sulfides and sulfoxides were for the most part dictated by their solubilities. The concentrations used for the sulfoxide Hammett studies were as follows: [PhSOEt]/[$Ph_2SO$]/[$(pXPh)_2SO$], X = MeO, 0.066 M/0.011 M/0.012 M; X = Me, 0.064 M/0.103 M/0.103 M; X = Cl, 0.064 M/0.022 M/0.018 M; X = $NO_2$, 0.062 M/0.022 M/0.006 M. The concentrations used for sulfide Hammett studies were as follows: [PhSOEt]/[$Ph_2S$]/[$(pXPh)_2S$], X = MeO, 0.071 M/0.051 M/0.050 M; X = Me, 0.102 M/0.052 M/0.052 M; X = Cl (run 1) 0.101 M/0.051 M/0.060 M (run 2) 0.101 M/0.050 M/0.052 M; X = $NO_2$, 0.103 M/0.051 M/0.058 M. The solutions containing the two competing substrates were transferred into glass tubes and sealed with a septum and placed on a merry-go-round. The samples were irradiated through a 12 M $NaNO_2$ filter solution[23] with a 400 W medium-pressure Hanovia lamp. Aliquots (130–140 $\mu$L) were removed at six different irradiation times and diluted to 1 mL with benzene. The irradiation times were chosen to ensure less than 10% conversions of both the sulfenate ester and the trapping agents. The percent conversion only exceeded this limit in the case of trapping with $(p\text{-}NO_2Ph)_2SO$ where data from percent conversions as high as 18.1% were used in the calculations. The concentrations of products were determined using calibration curves together with areas determined on a Perkin-Elmer Autosystem capillary gas chromatograph. The GC conditions were as follows: initial temperature 75 °C, isothermal time 3 min, first ramp rate 8 °C/min to 200 °C, isothermal time 4 min, second ramp rate 10 °C/min to 250 °C, He flow rate 0.6 to 0.8 mL/min and injector temperature 230 °C. By use of these conditions the retention times were as follows: biphenyl, 17.3 min; PhSOEt, 13.5 min; $PhSO_2Et$, 16.3 min; $PhSO_3Et$, 18.1 min; $(p\text{-}XPh)_2S$, X = MeO, 32.9 min, X = Me, 26.6 min, X = H, 21.6 min, X = Cl, 29.3 min, X = $NO_2$, 51 min; $(p\text{-}XPh)_2SO$, X = MeO, 44.6 min, X = Me, 32.8 min, X = H, 27.5 min, X = Cl, 35.3 min, X = $NO_2$, 64.1 min, $(p\text{-}XPh)SO_2$; X = MeO, 48.5 min, X = Me, 34.4 min, X = H, 28.5 min, X = Cl, 35.5 min, X = $NO_2$, 58.5 min. The values of $k_X/k_H$ were determined using the following equation in which $x = 0$ for sulfides and $x = 1$ for sulfoxide:

$$\ln\left(1 - \frac{[(\mathrm{pXPh})_2\mathrm{SO}_{x+1}]}{[(\mathrm{pXPh})_2\mathrm{SO}_x]_o}\right) = \frac{k_X}{k_H}\ln\left(1 - \frac{[(\mathrm{Ph})_2\mathrm{SO}_{x+1}]}{[(\mathrm{Ph})_2\mathrm{SO}_X]_o}\right)$$

**$k_T$ Determination.** The $k_T$ measurement was done in benzene using the apparatus and procedure previously described.[4] The concentration of **1** was chosen in order to observe decreases in the lifetime of singlet oxygen over a range of approximately 25–15 $\mu$s. The $k_T$ value was obtained from the experimental lifetimes by plotting $k_{obsd}$ versus the concentration of **1** used for the particular experiment. The $k_T$ value was determined twice with a precision of ±15%.

**$k_r$ Determination.** Two solutions, one containing 0.18 M **1**, $1.8 \times 10^{-2}$ M biphenyl, and $4 \times 10^{-5}$ M TPP, and the second containing 0.15 M **3**, $1.75 \times 10^{-2}$ M biphenyl, and $4 \times 10^{-5}$ M TPP, were saturated with oxygen and placed on a merry-go-round and irradiated with a 400 W medium-pressure Hanovia lamp modified by a 12 M $NaNO_2$ filter solution. Aliquots were removed and analyzed by the autosampler GC, and the concentrations of the reaction components were determined using predetermined calibration curves. The concentrations of **1** used in Figure 2 were determined by subtracting the concentrations of the oxidation products from the initial concentration of **1** (0.18 − [$PhSO_2Et$] − [$Ph_2SO_3$]). The concentrations of **3** used in Figure 2 were determined by subtracting one-half of the adamantanone, which forms quantitatively by decomposition of the dioxetane on the GC column, and a small amount of epoxide which forms in each reaction from the starting concentration of **3** (0.15 − 1/2[adamantanone] − [**3** − epoxide]). The $k_r$ was determined by multiplying the slope of the least squares line in Figure 2 by $k_T$ for **3** ($3.49 \times 10^5$ M$^{-1}$ s$^{-1}$).

**Sulfide and Sulfoxide Trapping.** The trapping studies were conducted in oxygen-saturated benzene solutions containing **1**, $Ph_2S$ or $Ph_2SO$, 3–4 × $10^{-5}$ M TPP, and either $1.06 \times 10^{-3}$ or $9.74 \times 10^{-3}$ M biphenyl. These samples were irradiated with either a 500 W tungsten–halogen or 400 W medium-pressure Hanovia lamp through a 1 cm thick 75% w/v $NaNO_2$ filter solution. The studies done with the Hanovia lamp were conducted on a merry-go-round in sealed ampules. The studies conducted with the tungsten–halogen lamp were conducted using samples continually agitated with bubbling oxygen. The concentrations of the products were monitored by capillary GC using the same experimental conditions reported above for the Hammett studies. The maximum conversions of the sulfenate ester were kept to less than 15%. Even at these low conversions the sulfinate ester appears to compete with $Ph_2SO$ and $Ph_2S$ for the intermediate, and small amounts of **1SO$_2$** are formed in several cases. In the $Ph_2S$ trapping studies 6.4% of **1SO$_2$** was formed in one case but in general less than 2% of **1SO$_2$** was observed and even less in the $Ph_2SO$ trapping experiments. As a consequence, the adventitious formation of **1SO$_2$** in these experiments had little or no effect on the experimental results. The ratios [$PhSO_2Et$]/[$Ph_2SO$] and [$PhSO_2Et$]/[$Ph_2SO_2$] were determined from the slopes of plots of [$PhSO_2Et$] versus [$Ph_2SO$] and [$Ph_2SO_2$] which were constructed by taking a minimum of 5 aliquots during various times of the irradiation.

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[21] Moore, T. L.; O'Connor, D. E. *J. Org. Chem.* **1966**, *31*, 3587–3592.

[22] Ethyl benzenesulfinate; *Beilsteins' Handbook of Organic Chemistry*; **11**, 6a, **III**, 4a. Ethyl benzenesulfonate; *Beilsteins' Handbook of Organic Chemistry*; **11**, 30b, **I**, 11a, **II**, 20b, **III**, 36b, **IV**, 30.

[23] Parker, C. A. *Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry*; Elsevier, Inc.: New York, 1968.