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Reaction of Singlet Oxygen with Thietane. A Novel Example of a Self-Catalyzed Reaction Which Provides Evidence for a Thiadioxirane Intermediate

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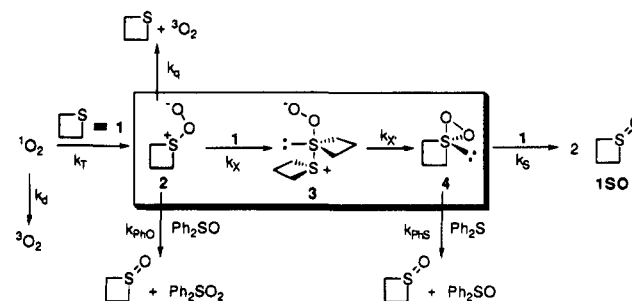
Abstract: Singlet oxygen reacts with thietane, **1**, to give the sulfoxide, **ISO**, and a trace of sulfone, **ISO₂**. A mechanism which involves a novel substrate catalyzed interconversion of a persulfoxide and thiadioxirane intermediate is proposed. The data which support the reaction of the persulfoxide with **1** by attack at sulfonium sulfur include the facts that Ph₂SO and **1** compete for a common intermediate and physical quenching is suppressed by increasing concentrations of **1**. The unique ability of **1** to catalyze its own oxidation is a result of a small C–S–C angle which allows an unencumbered approach to the sulfonium sulfur. In contrast, the larger C–S–C angle in Et₂S sterically precludes the catalysis step and forces direct collapse of the persulfoxide to the thiadioxirane intermediate.

In 1983, 30 years after the first report of the photooxidation of a dialkyl sulfide,¹ Foote and co-workers² suggested a mechanism for the reaction of singlet oxygen (¹O₂) with diethyl sulfide (Et₂S) which has served as the prototypical example for sulfide photooxidation reaction surfaces. The unique feature of the Foote mechanism was the suggestion of two intermediates, a persulfoxide which collapsed to the second intermediate in competition with physical quenching, and a thiadioxirane which reacts with a molecule of substrate to give the sulfoxide product. Recently, however, concerns about the viability of the second intermediate on the Foote reaction surface have called into question the generality of this mechanism and have pointed out the need for more detailed kinetic studies with other dialkyl sulfides.^{3,4} We report here the first extensive study of the photooxidation of a cyclic sulfide, thietane **1**, and compare it to the photooxidation of Et₂S. We also suggest a new mechanism for the photooxidation of **1** which differs from the Foote mechanism for Et₂S in that it invokes a novel substrate-catalyzed interconversion of persulfoxide **2**, and thiadioxirane **4**, intermediates.

Photooxidations of **1** (0.05–0.2 M) in oxygen-saturated CDCl₃ solutions containing (2–4) × 10^{−5} M TPP (tetraphenylporphyrin) as sensitizer were conducted at room temperature by irradiation with a 650-W tungsten–halogen or a 450-W medium-pressure Hg lamp through a 1-cm NaNO₂ filter solution. Under these carefully controlled conditions the sulfoxide, **ISO**, and a trace of the sulfone, **ISO₂**, were the only products observed at either high or low conversions.⁵ Identical results were also obtained in benzene and in acetone-*d*₆ at both room and low temperatures. The experimental evidence which supports the mechanism for this photooxidation as outlined in Scheme 1 includes the following:

(1) Cophotooxidations of **1** with diphenyl sulfoxide (Ph₂SO) and diphenyl sulfide (Ph₂S) produce diphenyl sulfone (Ph₂SO₂) and Ph₂SO, respectively. Control reactions demonstrate that Ph₂SO and Ph₂S are inert to singlet oxygen under the reaction

Scheme 1



conditions and provide evidence for the trapping of an intermediate. Furthermore, Hammett trapping studies with a series of diaryl sulfoxides and sulfides provide compelling evidence for the presence of at least two intermediates with ρ values of +1.05 and −1.26, respectively.⁶

(2) A quantitative treatment of Ph₂SO trapping at low conversions of **1** (<15%) demonstrates that a plot of [ISO]/[Ph₂SO₂] versus 1/[Ph₂SO] is linear with a slope which is

(5) The amount of sulfone formed is a function of both the solvent and temperature. In acetone at −78.5 °C **ISO₂** was approximately 2% of the reaction mixture after 2 min and only 3% of the reaction mixture after 30 min of irradiation. In acetone at 16 °C, however, the sulfone was not detected after 2 min and was present only to the extent of 2% after 30 min of irradiation. In benzene, where much of the work reported in this manuscript was conducted, **ISO₂** was 2% of the reaction mixture after 2 min and 7.5% of the reaction mixture after 30 min of irradiation. The small amount of sulfone formed in the reaction of **1** makes a mechanistic study difficult at best. However, oxygen labeling studies with Et₂S reveal that both oxygen atoms originated from the same oxygen molecule (Clennan, E. L.; Zhang, H. J. *Org. Chem.* 1994, 59, 7952–7954), suggesting that **ISO₂** is formed by adventitious trapping of an intermediate by **ISO** formed in the reaction. Regardless of its origin we do not believe that the formation of **ISO₂** affects the kinetic arguments presented in this paper.

(6) The observation of two different Hammett ρ values does not by itself require the presence of two intermediates since it is possible for a single intermediate to behave as a nucleophile toward one reagent and as an electrophile toward another. This could especially be true for zwitterionic persulfoxides or persulfoxides with substantial diradical character as has been claimed for some carbonyl oxides. (Yamaguchi, K.; Takada, K.; Otsuji, Y.; Mizuno, K. In *Organic Peroxides*; Ando, W., Ed.; John Wiley & Sons: New York, 1992; pp 1–100). However, the similarity of these Hammett ρ values to those measured for Et₂S photooxidation (+1.41 and −1.25) (E. L. Clennan, A. Greer, unpublished results) where the trapping of different intermediates has been kinetically demonstrated argues against this possibility.

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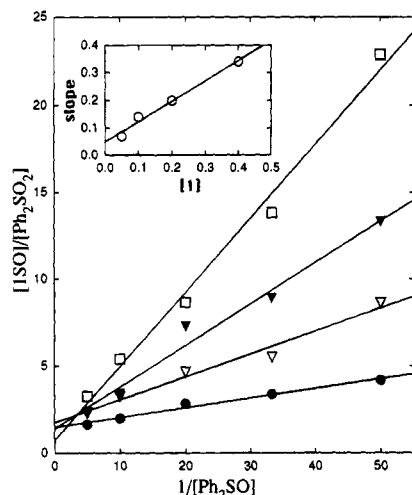


Figure 1. Diphenyl sulfoxide trapping of an intermediate in the photooxidation of **1** in benzene: ●, $[1] = 0.05$ M, slope = 0.07 ± 0.02 , $r = 0.9901$; ▽, $[1] = 0.10$ M, slope = 0.14 ± 0.02 , $r = 0.9872$; ▼, $[1] = 0.20$ M, slope = 0.20 ± 0.04 , $r = 0.9895$; □, $[1] = 0.40$ M, slope = 0.34 ± 0.05 , $r = 0.9947$. Inset: (slope)' = 0.74 , $r = 0.9927$.

dependent on the concentration of **1** (Figure 1). The sensitivity of the slope to the concentration of **1** is consistent with competitive trapping of an intermediate by **1** and Ph_2SO as shown by eq 1, which was derived by treating persulfoxide **2**, sulfide-complexed persulfoxide **3**, and thiadioxirane **4**, in Scheme 1, in terms of the steady state approximation.² In addition, the direct proportionality between the slopes of Figure 1 and $[1]$ is realized as shown in the inset of Figure 1. The calculated value for k_X/k_{PhO} from this figure is 0.37 and is more than 16 times larger than the same value reported for Et_2S photooxidation (0.023), consistent with the suggestion that **1** acts as a catalyst for the interconversion of **2** and **4**.

$$[\text{ISO}]/[\text{Ph}_2\text{SO}_2] = 1 + 2k_X[1]/(k_{\text{PhO}}[\text{Ph}_2\text{SO}]) \quad (1)$$

(3) The rate constants for disappearance of $^1\text{O}_2$ induced by interaction with both **1** and Et_2S , k_T , were measured in benzene by monitoring the ability of these substrates to quench its emission at 1270 nm^{7,8} and gave very similar values of $(3.13 \pm 0.22) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $(3.04 \pm 0.52) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively.^{9,10} However, the amount of product formed at a given time of irradiation under conditions where k_d (the rate constant defining the natural lifetime of $^1\text{O}_2$ in the solvent) is much less than $k_T[\text{R}_2\text{S}]$ (Scheme 1) is independent of substrate concentration during Et_2S photooxidation but dependent on substrate (Figure 2) concentration during the reaction of **1**. This unusual observation is consistent with competitive inhibition of physical quenching, k_p , by **1** but not by Et_2S . In addition, the change in the magnitude of k_T (the chemical rate constant at low conversion as measured by competition¹¹ with adamantylideneadamantane ($k_T = 3.49 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)¹²) as a function of $[1]$ can be quantitatively predicted using Scheme 1 and the corresponding eq 2 (inset in Figure 2). This plot demonstrates

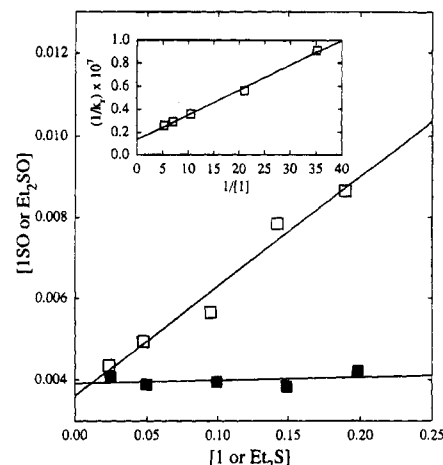


Figure 2. Concentration of oxidized photoproducts from the photooxidations of **1** and Et_2S as a function of their concentrations in benzene at low conversion (<20%): ■, Et_2S ; □, **1**. Inset: $1/k_T$ for the photooxidation of **1** as a function of $[1]^{-1}$. Intercept = $1.3452 \times 10^{-8} \text{ M s}$, slope = $2.1569 \times 10^{-9} \text{ M}^2 \text{ s}$, $r = 0.9977$.

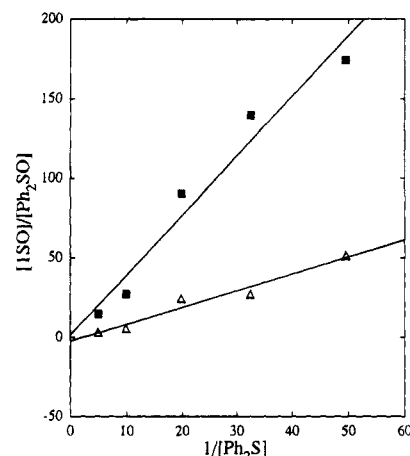


Figure 3. Diphenyl sulfide trapping of an intermediate in the photooxidation of **1** in benzene: △, $[1] = 0.02$ M, slope = 1.057 , $r = 0.9784$; ■, $[1] = 0.10$ M, slope = 3.757 , $r = 0.9787$.

that as the concentration of **1** is increased from 0.028 M to 0.19 M, the contribution of physical quenching to the total interaction of **1** with $^1\text{O}_2$ decreases from 85 to 48%. Furthermore, the value of k_T ($3.71 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) obtained from the intercept of this plot is remarkably close to the value independently measured for k_T (vide supra).

$$1/k_T = 1/(2k_T) + k_q/(2k_Xk_T[1]) \quad (2)$$

(4) A quantitative treatment of Ph_2S trapping at low conversions of **1** (<15%) gives a plot of $[\text{ISO}]/[\text{Ph}_2\text{SO}]$ versus $1/[\text{Ph}_2\text{S}]$ which is linear with a slope dependent on the concentration of **1** (Figure 3) consistent with the trapping of **4** (Scheme 1) as described by eq 3.² The value of k_S/k_{PhS} deduced from this plot (22.38) is very similar to that reported for Et_2S photooxidation (17.63), consistent with the conclusion that similar intermediates, presumably thiadioxiranes, are trapped in both systems. Furthermore, a thiadioxirane is a more reasonable candidate than either **2** or **3** for the electrophilic species trapped in the Hammett studies (vide supra).

$$[\text{ISO}]/[\text{Ph}_2\text{SO}] = 1 + 2k_S[1]/(k_{\text{PhS}}[\text{Ph}_2\text{S}]) \quad (3)$$

(5) The amount of product formation at a given time of irradiation under conditions where $k_d \ll k_T[\text{R}_2\text{S}]$ (Scheme 1) is

(7) Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. J. *Org. Chem.* **1989**, *54*, 3581–3584.

(8) Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080–5085.

(9) Foote has previously reported $k_T = 1.71 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ by an indirect method. Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765–769.

(10) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761–764.

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

(12) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809–810.

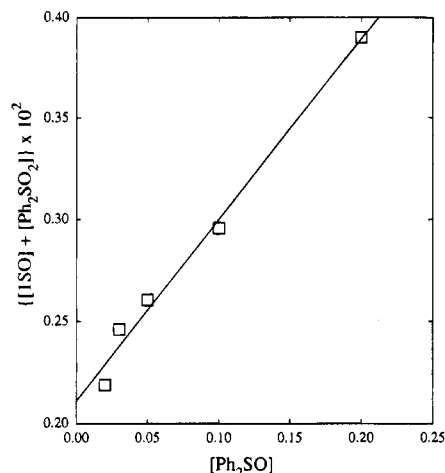
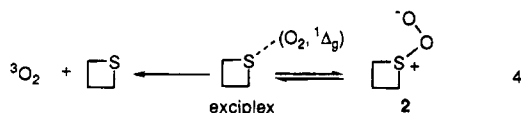


Figure 4. Product yield in the photooxidation of **1** as a function of $[\text{Ph}_2\text{SO}]$ at a given time of irradiation.

a function of the concentration of the additive Ph_2SO (Figure 4). This observation demands that physical quenching of singlet oxygen, k_q , occurs subsequent to the irreversible formation of the trapped persulfoxide intermediate, **2**. Alternatively, physical quenching could occur by decomposition of an exciplex¹³ which is in equilibrium with the persulfoxide, **2** (eq 4). However, since these two mechanistic possibilities are kinetically indistinguishable, we have chosen for simplicity to represent physical quenching by decomposition of the covalently bound intermediate, **2** (Scheme 1). This decomposition is not in violation of spin conservation rules as a result of the presence of low-lying d-orbitals on sulfur.



These data taken together provide a compelling argument for the mechanism suggested in Scheme 1. In addition, they also provide strong circumstantial evidence for the existence of a thiadioxirane on the reaction surface, since the catalysis, as revealed by the larger magnitude of k_X/k_{PhO} for **1** in comparison to Et_2S , can be viewed as a preorganization of the persulfoxide, **2**, into the 4-coordinate geometry adopted by the thiadioxirane, **4**. In the absence of this catalysis internal geometric reorganization and the increase in strain accompanying three-membered ring formation occurs in one energetically demanding rather than in two microscopic steps.

We believe that the unique ability of **1** to catalyze its own oxidation is a result of a small C–S–C angle of 78° ¹⁴ which allows an unencumbered approach to the sulfonium sulfur in **2**. In contrast, the larger C–S–C angle in Et_2S , 98.9° ,¹⁴ sterically precludes the catalysis step and forces a unimolecular collapse of the persulfoxide, **2**, directly to the thiadioxirane, **4**.

Experimental Section

General Aspects. Gas chromatographic data were collected on one of three gas chromatographs, a Hewlett-Packard GC/MS instrument consisting of a 5890 series II GC and a 5971 series mass selective detector, on a Perkin-Elmer Autosystem, or on a Perkin-Elmer 8500

capillary gas chromatograph. The GC column used for all the work was a HP-5 [30 m × 0.25 mm (or 0.53 mm for the Perkin-Elmer instruments) × 0.25 μm (length × inside diameter × film thickness)] capillary column. Calibration curves were constructed for **ISO**, **ISO**₂, and all the substituted sulfoxides, and sulfones using authentic samples. Thietane, **1**, was obtained from Aldrich and distilled from KOH prior to use. Adamantanone (99%) and TPP were obtained from Aldrich and used without further purification. Adamantylideneadamantane was synthesized and purified as reported in the literature.¹⁵ Biphenyl was used as received. Diphenyl sulfide (Aldrich, 98%) was distilled under reduced pressure (b 124 °C/6 mmHg). Diphenyl sulfoxide was recrystallized from hexane–methylene chloride or hexane–ethyl acetate and its purity checked by GC prior to use. Benzene was distilled from P_2O_5 .

k_r Determinations. The k_r determinations were conducted in 1-mL benzene solutions containing 2×10^{-4} M TPP, 0.159 M adamantylideneadamantane, and concentrations of **1** from 0.028 to 0.142 M. The samples were irradiated with a 500-W tungsten–halogen lamp modified by a 1 cm path length 12 M NaNO_2 solution (400 nm cutoff). Aliquots were removed from the reaction vessels at 30, 45, 60, 75, 90, 105, 120, and 140 s and analyzed by gas chromatography. The conversions of **1** were kept to less than 15% and the conversions of adamantylideneadamantane to less than 1%. The concentrations of the reaction components were determined from calibration curves determined using authentic samples of **ISO** and adamantanone and by setting $[\text{AdAdO}_2] = 0.5 \times [\text{adamantanone}]$. The rate constant for product formation from **1** relative to the rate constant for dioxetane formation from adamantylideneadamantane $k_r(\text{1})/k_r(\text{AdAd})$ was calculated using an equation derived by Higgins, Foote, and Cheng.¹⁶ The $k_r(\text{1})$ values were determined by multiplying the slopes of these plots by the previously determined value of $k_r(\text{AdAd})$.^{12,17}

Hammett Studies. The sulfoxide and sulfide Hammett studies were conducted in oxygen-saturated benzene solutions containing 0.1 M **1**, 6×10^{-4} M biphenyl as an internal standard, 5×10^{-5} M TPP, 0.05 M Ph_2SO , and 0.05 M $(p\text{XPh})_2\text{SO}$ (or 0.05 M Ph_2S and 0.05 M $(p\text{XPh})_2\text{S}$ for the sulfide Hammett plot) ($p\text{XPh} \equiv p\text{-XC}_6\text{H}_4$). The samples were irradiated on a merry-go-round with a 400-W medium-pressure Hanovia lamp modified with a 1-cm filter solution consisting of 12 M NaNO_2 . Aliquots were removed at times selected in order to ensure less than 15% conversion of any reaction component, and the ratios k_X/k_H were determined from the slopes of plots of $[(p\text{XPh})_2\text{SO}_2]$ versus $[\text{Ph}_2\text{SO}_2]$ or plots of $[(p\text{XPh})_2\text{SO}]$ versus $[\text{Ph}_2\text{SO}]$. These concentrations were determined immediately after photolysis by gas chromatography using predetermined calibration curves for authentic samples of the sulfones and sulfoxides.

Diphenyl Sulfoxide Trapping Studies. The sulfoxide trapping studies were conducted in 0.5 mL of spectral grade benzene in 5-mm NMR tubes containing 5×10^{-5} M TPP and various concentrations of **1** and Ph_2SO . Oxygen was bubbled into the solutions during and for 20 min prior to the irradiations of the samples with a 500-W tungsten–halogen lamp. A 12 M NaNO_2 filter solution (1-cm path length) was used to ensure exclusive irradiation of the sensitizer. Aliquots were removed at times selected to ensure less than 15% conversions of **1**, and the ratio $[\text{ISO}]/[\text{Ph}_2\text{SO}_2]$ was determined from the slopes of plots of $[\text{ISO}]$ versus $[\text{Ph}_2\text{SO}_2]$. The concentrations of **ISO** and Ph_2SO_2 were determined by GC with the aid of predetermined calibration curves constructed for authentic samples.

Diphenyl Sulfide Trapping Studies. The diphenyl sulfide trapping studies were conducted in a manner identical to that reported above for the diphenyl sulfoxide trapping experiments except in 10-mL Pyrex test tubes.

Concentration Studies. The data used to generate Figure 2 were collected at 20 °C. Irradiations of 1.0-mL benzene solutions containing various concentrations of **1** or Et_2S , 5×10^{-5} M TPP, and 6×10^{-4} M biphenyl were conducted with a 400-W medium-pressure Hanovia lamp

(13) Direct spectral evidence for the structure of intermediate **2** does not exist, and either a covalently or a loosely bound complex (exciplex) is consistent with the experimental data. Gorman, A. A. In *Advances in Photochemistry*; Volman, D., Hammond, G., Neckers, D., Eds.; John Wiley & Sons: New York, 1992; Vol. 17, pp 217–274.

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(17) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218–4227.

through a NaNO_2 filter solution. The Et_2S samples were irradiated for 30 min and the samples of **1** for 15 min on a merry-go-round. The data used to generate Figure 4 were collected at 20 °C by irradiation of 1.0-mL benzene solutions containing various concentrations of Ph_2SO , 0.05 M **1**, 6×10^{-4} M biphenyl, and 5×10^{-5} M TPP. All the samples were irradiated on a merry-go-round for 4.5 min.

k_T Determination. The k_T value for **1** was obtained in benzene using the apparatus and procedure previously described.^{7,8} The concentrations of **1** were chosen in order to observe a decrease in the lifetime of singlet oxygen over a range of approximately 15–25 μs . 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 three times with a precision of $\pm 15\%$.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Appendix A. Derivation of Eq 2. Chemical Reaction Rate Determination

The measurements needed to construct the inset plot in Figure 2 were done in the absence of either Ph_2S or Ph_2SO and therefore using Scheme 1 as a reference:

$$\frac{d[\text{1SO}]}{dt} = 2k_S[\text{1}][\text{4}] \quad (\text{A})$$

Steady state approximation in **4** gives

$$\frac{d[\text{4}]}{dt} = 0 = k_X[\text{3}] - k_S[\text{1}][\text{4}]$$

$$[\text{4}] = k_X[\text{3}]/k_S[\text{1}] \quad (\text{B})$$

Steady state approximation in **3** gives

$$\frac{d[\text{3}]}{dt} = k_X[\text{1}][\text{2}] - k_X'[\text{3}]$$

$$[\text{3}] = k_X[\text{1}][\text{2}]/k_X' \quad (\text{C})$$

Steady state approximation in **2** gives

$$\frac{d[\text{2}]}{dt} = 0 = k_T[\text{1}][^1\text{O}_2] - k_X[\text{1}][\text{2}] - k_q[\text{2}]$$

$$[\text{2}] = k_T[\text{1}][^1\text{O}_2]/(k_X[\text{1}] + k_q) \quad (\text{D})$$

Combining eqs B and C gives

$$[\text{4}] = k_X[\text{2}]/k_S \quad (\text{E})$$

Combining eqs A and E gives

$$\frac{d[\text{1SO}]}{dt} = 2k_X[\text{1}][\text{2}] \quad (\text{F})$$

Combining eqs D and F gives

$$\frac{d[\text{1SO}]}{dt} = 2k_Xk_T[\text{1}]^2[^1\text{O}_2]/(k_X[\text{1}] + k_q) \quad (\text{G})$$

Set k_r equal to $2k_Xk_T[\text{1}]/(k_X[\text{1}] + k_q)$. Then

$$\frac{d[\text{1SO}]}{dt} = k_r[\text{1}][^1\text{O}_2] \quad (\text{H})$$

and

$$1/k_r = 1/2k_T + k_q/(2k_Xk_T[\text{1}]) \quad (2)$$

At very low conversion of **1** ($\leq 15\%$) k_r will be effectively a constant and equation H can be used in conjunction with the Higgins and Foote¹⁶ competitive approach to determine the magnitudes of k_r at various concentrations of **1**. Experimentally one obtains from eq 2 slope/intercept = $k_q/k_X = 0.16$.

Supporting Information Available: Hammett plots for the diaryl sulfoxide and sulfide trapping (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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