

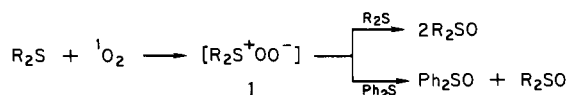
Chemistry of Singlet Oxygen. 35. Nature of Intermediates in the Photooxygenation of Sulfides

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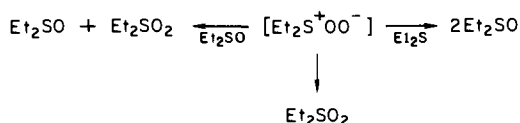
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Several reports of the trapping of primary peroxidic intermediates in the reaction of $^1\text{O}_2$ with organic molecules have appeared.¹⁻⁹ Foote and Peters^{2,3} suggested that the primary product of sulfide photooxygenation is a zwitterionic peroxide (a "per-sulfoxide", **1**) which results from the nucleophilic attack of the sulfide on $^1\text{O}_2$.¹⁰ They presented evidence that this intermediate could be trapped by various agents. Among these was diphenyl sulfide, itself unreactive toward $^1\text{O}_2$, which gave diphenyl sulfoxide and dialkyl sulfoxide as products of the trapping reaction. Since then, the nature of intermediate **1** has been of interest.^{9,11-13} We now report preliminary results of a systematic investigation of the trapping of **1** by sulfoxides, which prove to be surprisingly good trapping agents, and show that a new reaction course must be proposed for the reaction in aprotic solvents.



Relative Trapping Ability of Sulfoxides and Sulfide. When Et_2S was photooxidized in benzene in the presence of Ph_2S , Ph_2SO , and Me_2SO , various amounts of trapping products (Ph_2SO , Ph_2SO_2 , and Me_2SO_2 , respectively) were formed (Table I). The results in Table I translate into trapping abilities of 1:51:6 for Ph_2S - Ph_2SO - Me_2SO . The ratio of the relative trapping abilities of Ph_2S and Ph_2SO changed to 1:4.6 in favor of Ph_2SO when methanol was the solvent. Controls showed that both Ph_2SO and Me_2SO are nearly inert toward $^1\text{O}_2$ under the conditions. Thus, it is clear that Ph_2SO reacts faster with the sulfide photooxidation intermediate than Ph_2S , but the difference is much larger in benzene than in methanol.

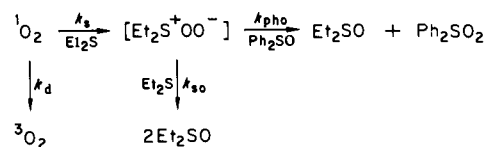
Since sulfoxides are such good traps for the intermediate, it became important to establish whether trapping of the intermediate by the product sulfoxide was the source of the sulfone product found^{2,3} in these reactions. While space does not permit a detailed discussion, we conclude that both this process and the direct rearrangement of the intermediate can contribute to the formation of sulfone, which is small in methanol but larger in aprotic solvents; however, the trapping by product can easily be suppressed by keeping conversions low.



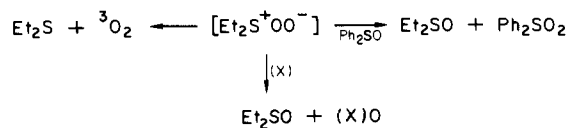
Kinetics of Ph_2SO Trapping^{14a} If the mechanism of the

- (1) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 7771.
- (2) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.
- (3) Foote, C. S.; Peters, J. W. *IUPAC Congr.*, *23rd, Special Lect.* **1971**, *4*, 129.
- (4) Foote, C. S.; Fujimoto, T.; Chang, Y. C. *Tetrahedron Lett.* **1972**, 45.
- (5) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381.
- (6) Hasty, N. M.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380.
- (7) Schaap, A. P.; Faler, G. R.; Villasenor, S. R.; Zaklika, K. A., unpublished work.
- (8) Adam, W.; Rodriguez, R. *J. Am. Chem. Soc.* **1980**, *102*, 404.
- (9) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191.
- (10) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765.
- (11) Martin, L. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511.
- (12) Bartlett, P. D.; Aida, T.; Chu, H.-K.; Fang, T.-S. *J. Am. Chem. Soc.* **1980**, *102*, 3515.
- (13) Ando, W.; Kabe, Y.; Kobayashi, S.; Takyu, C.; Yamagishi, A.; Inaba, H. *J. Am. Chem. Soc.* **1980**, *102*, 4526.

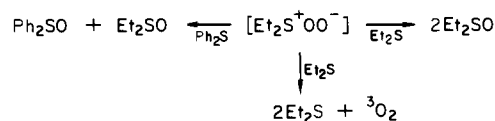
Scheme I



Scheme II



Scheme III



trapping by Ph_2SO of **1** is similar to that reported for Ph_2S ,^{2,3} and if the conversion is kept low enough and a large enough amount of Ph_2SO is used that trapping of **1** by product Et_2SO can be neglected, Scheme I can be derived.^{14b} If steady-state kinetics is assumed, Scheme I leads to eq 1.

$$\frac{[\text{Et}_2\text{SO}]}{[\text{Ph}_2\text{SO}_2]} = 1 + \frac{2k_{so}[\text{Et}_2\text{S}]}{k_{pho}[\text{Ph}_2\text{SO}]} \quad (1)$$

Figure 1 has plots of the data plotted according to eq 1 in both benzene and methanol. The observed behavior in methanol follows that predicted by eq 1 well (slope proportional to $[\text{Et}_2\text{S}]$). However, to our surprise, no such dependence on $[\text{Et}_2\text{S}]$ was observed in benzene.

Furthermore, if Scheme I holds, the formation of Ph_2SO_2 (the trapping product) should follow eq 2; a plot of the data according

$$[\text{Ph}_2\text{SO}_2]^{-1} = K^{-1} \left(1 + \frac{k_d}{k_s[\text{Et}_2\text{S}]} \right) \left(1 + \frac{k_{so}[\text{Et}_2\text{S}]}{k_{pho}[\text{Ph}_2\text{SO}]} \right) \quad (2)$$

to this relationship is shown in Figure 2. Since $k_d/k_s[\text{Et}_2\text{S}]$ is $\ll 1$,¹⁵ eq 2 predicts a straight line of slope proportional to $[\text{Et}_2\text{S}]$.^{14b} It is obvious that the predicted behavior is again shown in methanol

(14) (a) Detailed kinetic analysis will be presented in a full paper. (b) Photolyses were performed in a merry-go-round apparatus using a 1% aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ filter solution and a Sylvania DWY lamp. The sensitizer was zinc tetraphenylporphine (C_8H_6) or Rose Bengal (CH_3OH). Product concentrations after a given time were measured gas chromatographically (flame ionization, internal standard);^{2,3} low conversions were readily measured (see Tables I and II and Figures 1 and 2 for typical concentrations and conversions). Because conversions were kept low, $[\text{Et}_2\text{S}]$ could be treated as a constant, allowing the differential equation to be approximated as shown. Although at the highest conversions used, the approximation is not strictly valid, the deviation is small and does not affect the conclusions. Derivation of eq 1 (similarly for eq 2-4):

$$0 = d(^1\text{O}_2)/dt = K - (k_1[\text{Et}_2\text{S}] + k_d)[^1\text{O}_2]$$

where K = rate of formation of $^1\text{O}_2$. Thus

$$[^1\text{O}_2] = K/(k_1[\text{Et}_2\text{S}] + k_d)$$

Under the above conditions

$$[\text{Et}_2\text{SO}]_t \propto d(\text{Et}_2\text{SO})/dt = 2k_{so}[\text{Et}_2\text{S}] + k_{pho}[\text{Ph}_2\text{SO}]$$

and

$$[\text{Ph}_2\text{SO}_2]_t \propto d(\text{Ph}_2\text{SO}_2)/dt = k_{pho}[\text{Ph}_2\text{SO}]$$

Dividing,

$$\frac{[\text{Et}_2\text{SO}]}{[\text{Ph}_2\text{SO}_2]_t} \approx 1 + \frac{2k_{so}[\text{Et}_2\text{S}]}{k_{pho}[\text{Ph}_2\text{SO}]}$$

(15) Since for all the experiments performed, $[\text{Et}_2\text{S}] \geq 0.02$ M and k_d/k_s in benzene equals 1.96×10^{-3} M,¹⁰ the term $k_d/k_s[\text{Et}_2\text{S}]$ is small compared to 1.

Table I. Relative Trapping Ability of Sulfide and Sulfoxides Toward Et₂S Photooxidation Intermediates

solvent	substrate concn, M [Et ₂ S]	trapping agent concn, M			product concn, M			relative trapping ability Ph ₂ S:Ph ₂ SO:(CH ₃) ₂ SO
		[Ph ₂ S]	[Ph ₂ SO]	[(CH ₃) ₂ SO]	[Ph ₂ SO]	[Ph ₂ SO ₂]	[(CH ₃) ₂ SO ₂]	
benzene	0.02	6.0 × 10 ⁻²			4.5 × 10 ⁻⁵			1:51:6
benzene	0.02		6.0 × 10 ⁻²			2.31 × 10 ⁻³		
benzene	0.02			6.0 × 10 ⁻²			2.7 × 10 ⁻⁴	
benzene			6.0 × 10 ⁻²		trace			
benzene				6.0 × 10 ⁻²		trace		
methanol	0.02	6.1 × 10 ⁻²			3.6 × 10 ⁻⁴			1:4.6
methanol	0.02		6.0 × 10 ⁻²			1.64 × 10 ⁻³		
methanol			6.0 × 10 ⁻²			trace		

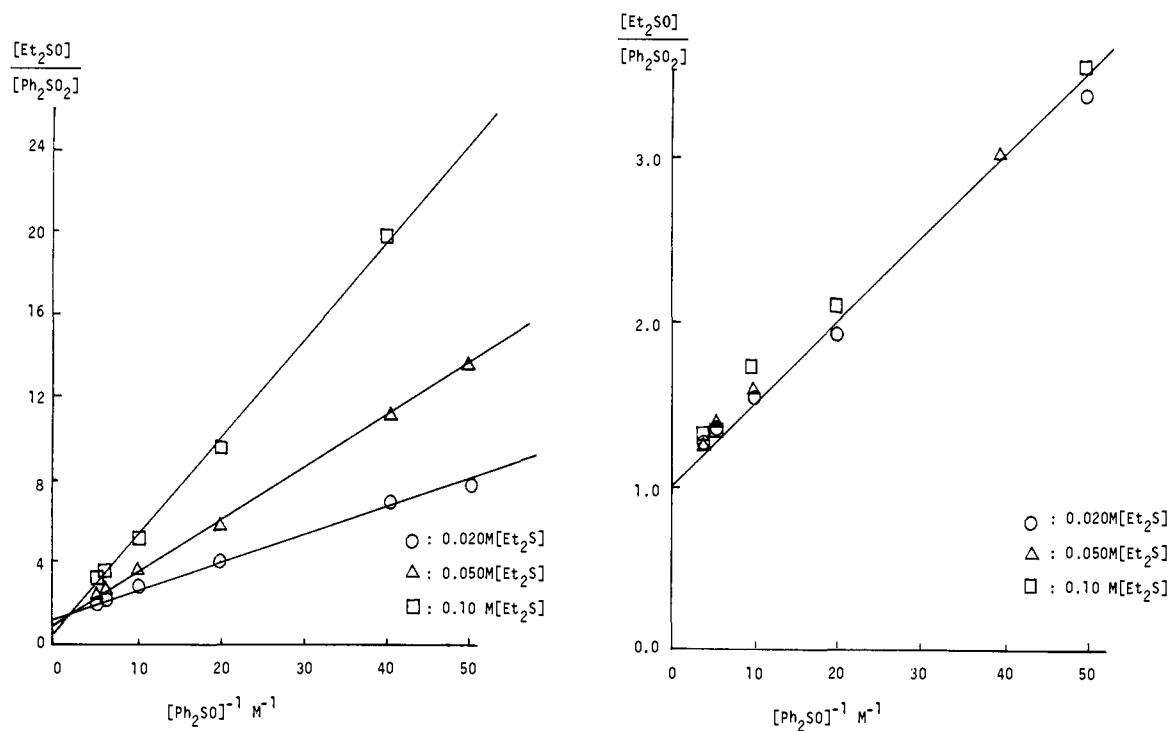
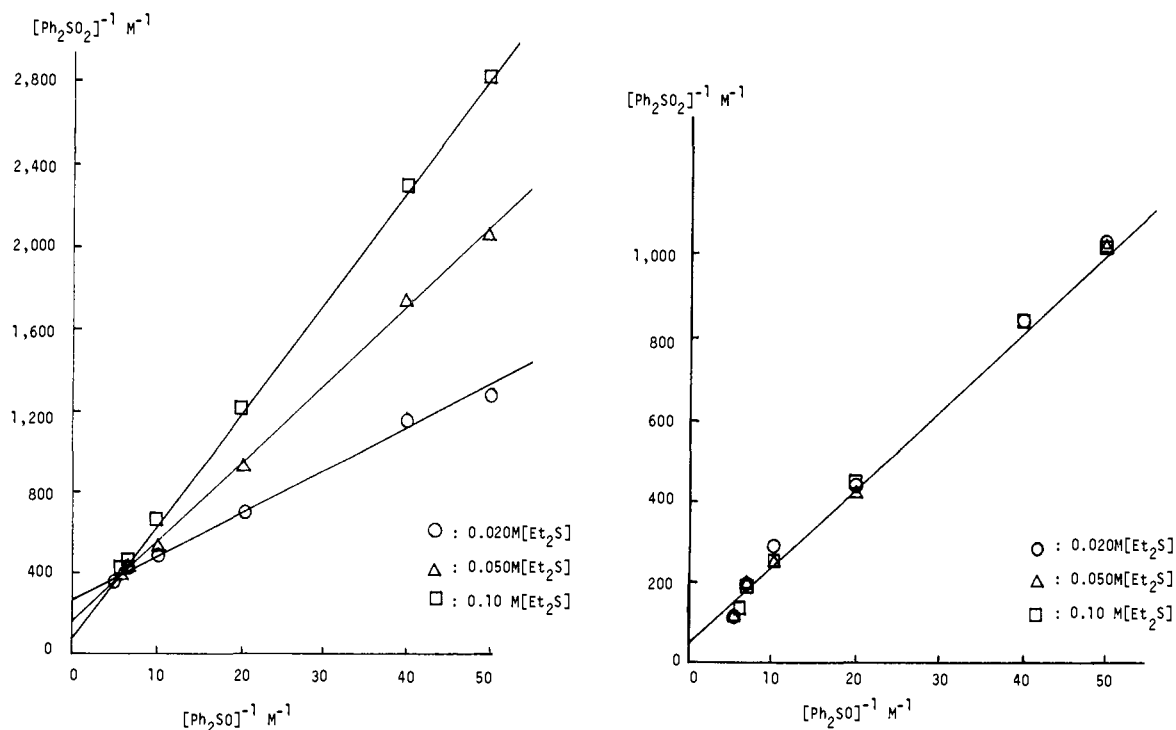
Figure 1. Kinetic behavior of Ph₂SO trapping of Et₂S photooxidation intermediates.Figure 2. Kinetic behavior of Ph₂SO trapping of Et₂S photooxidation intermediates.

Table II. Effect of Ph₂SO Trapping on Et₂SO Formation

[Ph ₂ SO], M	[Et ₂ SO] × 10 ³ M		
	[Et ₂ S] = 0.020 M	[Et ₂ S] = 0.050 M	[Et ₂ S] = 0.10 M
0.010	2.93	3.45	3.38
0.020	3.29	4.00	3.56
0.025		4.11	4.25
0.050	4.33	5.49	5.27
0.100	6.18	6.45	7.44
0.150	7.40	7.64	7.71
0.175			8.41
0.200	7.83	8.03	

but not in benzene (no [Et₂S] dependence of slope).

A modified scheme is obviously required to explain the behavior in benzene, where the amount of trapping depends on the concentration of the trap but not on that of diethyl sulfide; clearly, the two are not competing for a common intermediate in this solvent. A possible explanation for this behavior is that the primary intermediate can form sulfoxide without the intervention of a second sulfide molecule in this solvent (Scheme II). This explanation is also consistent with the otherwise very puzzling observation of Foote and Peters in benzene^{2,3} (where the majority of the removal of singlet oxygen does not lead to product) that the fraction of quenching does not depend on sulfide concentration. This behavior was very difficult to reconcile with Scheme 1;¹⁶ for an explanation of the observed kinetics, an implausible intervention of a second sulfide molecule in the quenching process was required (Scheme III). Under Scheme II, no sulfide concentration dependence of quenching is expected. From Scheme II, eq 3 and 4 follow:^{14b}

$$\frac{[\text{Et}_2\text{SO}]}{[\text{Ph}_2\text{SO}_2]} = 1 + \frac{2k_{so}}{k_{pho}[\text{Ph}_2\text{SO}]} \quad (3)$$

$$[\text{Ph}_2\text{SO}_2]^{-1} = K^{-1} \left(1 + \frac{k_d}{k_s[\text{Et}_2\text{S}]} \right) \left(1 + \frac{k_{so}}{k_{pho}[\text{Ph}_2\text{SO}]} \right) \quad (4)$$

According to eq 3, the slope of the plot of Figure 1 should be independent of [Et₂S], in agreement with the results in benzene. Also, since the term $k_d/k_s[\text{Et}_2\text{S}]$ in eq 4 can be neglected,¹⁵ the slope and intercept of Figure 2 should be independent of [Et₂S], as observed.

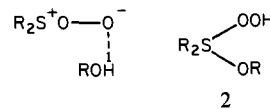
A prediction of Scheme II which was tested is that, in benzene, added Ph₂SO should increase the total amount of Et₂SO by suppressing the quenching step, since trapping and quenching are competitive. Table II shows that the expected relationship is observed.

Since Ph₂S traps the intermediate in benzene, and is only slightly less efficient than Et₂S (in methanol at least),^{2,3} why does Et₂S not compete kinetically for the intermediate? The answer can be seen from Table I: trapping by 0.06 M Ph₂S in the reaction of 0.02 M Et₂S actually gives only 4.5×10^{-5} M Ph₂SO. Thus, the trapping by sulfides is too inefficient to compete with decay of the intermediate in benzene. Only the more efficient sulfoxides can compete enough to affect the kinetics.

Although several more complex reactions have been considered and are not ruled out, Scheme II is the simplest which can explain our observations. Foote and Peters determined the stoichiometry of the reaction to be two sulfides per singlet oxygen in methanol.^{2,3} Peters¹⁷ reported that the stoichiometry of the reaction was also 2:1 in benzene. This stoichiometry is not consistent with Scheme II. However, the stoichiometry cannot be determined easily under conditions where some 96% of the ¹O₂ is quenched and only 4% gives product, as in benzene. A rationale for a change in stoichiometry is provided by the observation of Sawaki and Ogata¹⁸

that phenol is a minor product of the reaction: inefficient attack on solvent benzene by the intermediate could result in the formation of phenol and sulfoxide. Other mechanisms for the reduction of the intermediate to sulfoxide without the intervention of a second sulfide are also possible.

The effect of protic solvents on the reaction is to dramatically favor product formation at the expense of quenching, with very little effect on the total removal rate of ¹O₂.^{2,3,10} We have repeatedly confirmed this observation of Foote and Peters, who suggested that stabilization of the intermediate by methanol was responsible for the effect. An alternate possibility, that addition of methanol to the intermediate occurs to give a peroxy-sulfurane 2, similar to those proposed by Martin et al.,¹¹ seems less likely,



since this intermediate would be expected to oxidize sulfides much more readily than sulfoxides.¹⁸ From Table I, Ph₂SO is a better trap than Ph₂S, although less so than in methanol. These results parallel those of Sawaki and Ogata,¹⁸ who report the intermediate to be nucleophilic in benzene but less so in methanol. Further work on this interesting system will be the subject of several papers in the near future.^{19,20}

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(18) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.*, preceding paper in this issued. We thank Drs. Sawaki and Ogata for a prepublication copy of their manuscript.

(19) Taken in part from: Gu C.-L., Dissertation, University of California, Los Angeles, 1981. Kacher, M. L. Dissertation, University of California, Los Angeles, 1977.

(20) Note Added in Proof: A paper on sulfoxide trapping has just come to our attention: Cauzzo, G.; Gennari, G.; Da Re, F.; Curci, R. *Gazz. Chim. Ital.* 1979, 109, 541.

Observations on the Nature of Polylithium Organic Compounds and Their Rearrangements

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Recently, there has been increasingly widespread theoretical interest in the structures and properties of polylithium organic compounds.¹⁻⁶ This has been coupled with and, in some instances, stimulated by a substantial amount of synthetic work.⁷⁻¹⁰ The

(1) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 4332 (1976).

(2) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976).

(3) (a) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. A. Jorgensen, *Tetrahedron Lett.*, 3923 (1976); (b) E. D. Jemmis, D. Poppinger, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 5796 (1977); (c) G. Rauscher, T. Clark, D. Poppinger, and P. v. R. Schleyer, *Angew. Chem.*, **90**, 306 (1978); (d) E. D. Jemmis, J. Chandrasekhar, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **101**, 2848 (1979); (e) A. Kos, D. Poppinger, P. v. R. Schleyer, and W. Thiel, *Tetrahedron Lett.*, 2151 (1980).

(4) E. D. Jemmis, P. v. R. Schleyer, and J. A. Pople, *J. Organomet. Chem.*, **154**, 327 (1978).

(5) W. D. Laidig and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 5972 (1978).

(6) W. D. Laidig and H. F. Schaefer, *J. Am. Chem. Soc.*, **101**, 7184 (1979).

(16) Scheme I predicts that the fraction of quenching should increase as the Et₂S concentration decreases.

(17) Peters, J. W. *Dissertation*, University of California, Los Angeles, 1971.