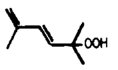
+ k_q) data from β values. These values depend on singlet oxygen lifetimes that were obtained by indirect methods;[47-49] reported values for the same solvent vary widely. Recent $^1O_2$ luminescence decay measurements provide more accurate and consistent $^1O_2$ lifetimes.[14-16] However, for solvents where $^1O_2$ is very long lived, consistent values are still difficult to obtain (for CCl_4 $^1O_2$ lifetimes of 26 000[14] and 900 μs[15] have been reported). Because of this problem and the fact that the data from CCl_4 and CS_2 (where $^1O_2$ is also long lived) are heavily weighted in Gollnick's plots, his transition-state dipole moment is likely to be seriously affected by these errors.

Finally, DMHD has also been reported to yield 2,5-dimethylhexa-1,3-diene 5-hydroperoxide, **12**, upon reaction with $^1O_2$ in a number of solvents.[49] The ratio **12**/**3** was reported to be as high as 9 in CCl_4 and 0.6 in BZ. We found that reaction of DMHD with $^1O_2$ in a C_6H_6;CCl_4 mixture (20% C_6D_6, 80% CCl_4 TPP = sensitizer) carried to low conversions (<10%) showed no sign of **12** by NMR; only **3** was detected. The NMR of **12** would show a distinctive doublet of doublets similar to its $(C_6H_5)_3P$ reduction product **12a** (isolated by preparative GC from photooxidation of DMHD run under acidic conditions, see Experimental Section). Also GC analysis after $(C_6H_5)_3P$ reduction showed only **3a**, and no **12a** (which had a shorter retention time). We believe the reported **12a** is probably formed by rearrangement of either the initial ene product **3** or the $(C_6H_5)P$ reduction product **3a** on TLC.



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Acknowledgment. This work was supported by NSF Grant No. CHE80-20140. Paper No. 43 in this series is is ref 1.

Registry No. **3a**, 85939-83-9; **5a**, 85939-84-0; 6, 85939-85-1; **12a**, 70254-39-6; 2M2P, 625-27-4; DMHD, 764-13-6; $^1O_2$, 7782-44-7.

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Chemistry of Singlet Oxygen. 45. Mechanism of the Photooxidation of Sulfides

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Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received December 6, 1982*

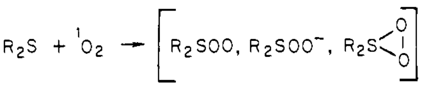
Abstract: The kinetics of the singlet oxygen oxidation of diethyl sulfide in the presence of diphenyl sulfoxide and diphenyl sulfide in various solvents (methanol, benzene, and acetonitrile) have been investigated. The results show that competitive trapping of a single intermediate species by diethyl sulfide, diphenyl sulfide, and diphenyl sulfoxide occurs in protic solvent (methanol), while in aprotic solvents (benzene, acetonitrile) only diphenyl sulfide competes with diethyl sulfide. Diphenyl sulfoxide traps an earlier intermediate; the same intermediate also leads to quenching. A mechanism is proposed in which an initial nucleophilic intermediate **2** can be trapped by electrophiles (diphenyl sulfoxide), lose singlet oxygen, or collapse to an electrophilic intermediate **3** that can be trapped by sulfide nucleophiles.

In the past two decades, there has been considerable interest in and intensive investigation of the photooxidation of sulfides.[1-12] The photosensitized deactivation of several enzymes such as phosphoglucomutase and chymotrypsin has been correlated with the photooxidation of methionine to the corresponding sulfoxide.[6,13-16]

The photooxidation of sulfides was first described by Schenck et al.[1,17,18] They reported that dialkyl sulfides undergo sensitized photooxidation to give 2 mol of sulfoxide per mol of absorbed oxygen.[1]

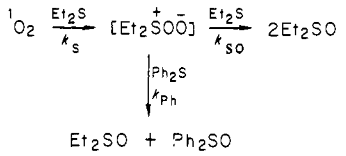
$$2R_2S + O_2 \xrightarrow[\text{sens}]{h\nu} 2R_2SO$$

A stepwise mechanism involving a reactive diradical intermediate, **1**, that reacts with a second sulfide to give the sulfoxide was proposed originally by Gollnick[1] in 1968. Foote et al,[5,6] suggested later that the intermediate might also be a persulfoxide, **2**, or a cyclic sulfurane, **3**, as shown.

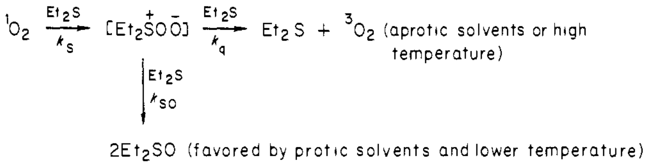


1 **2** **3**

Scheme I



Scheme II



A few years ago, Foote and Peters[2,5,6] reported that considerable diphenyl sulfoxide was produced along with diethyl sullfoxide when

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† Paper No. 44 in this series is: Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.*, in press.

(1) Krauch, C. H.; Hess, D.; Schenck, G. O., unpublished results; quoted by: Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

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(3) Skold, C. N,; Schlessinger, R. H. *Tetrahedron Lett.* **1970**, 791.

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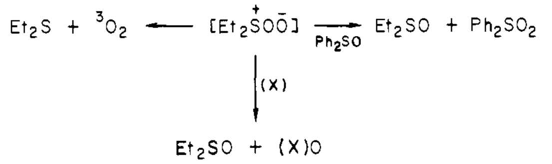
Scheme III



diphenyl sulfide, which is unreactive toward singlet oxygen, was added to the diethyl sulfide–${}^1O_2$ photooxidation in methanol. The proposed mechanism, shown in Scheme I, was consistent with the kinetics, which required competitive trapping of a single intermediate by these two sulfides.

Scheme I described the reaction well in methanol; however, it was not sufficient to fit the data obtained in aprotic solvents, in which the photooxidation of sulfide to sulfoxide proceeds very inefficiently. In benzene, kinetic analysis showed that over 95% of the reaction of singlet oxygen with diethyl sulfide results in nonreactive quenching of ${}^1O_2$ and only a few per cent leads to sulfoxide (no quenching of ${}^1O_2$ by diethyl sulfide occurs in methanol), and the quenching to oxidation ratio is independent of the sulfide concentration. In addition, the reaction in aprotic solvents speeds up dramatically as the temperature is decreased. In contrast, the overall rate at which singlet oxygen is removed is about the same in both benzene and methanol and is temperature independent.[5,19b] These effects were explained by incorporating a quenching process that involved interaction of the intermediate with a second sulfide molecule as shown in Scheme II; however, there was no rationale for this interaction, which was added only to account for the independence of the degree of quenching on sulfide concentration. The quenching process is suppressed in methanol and at lower temperatures in favor of product formation.[19]

In a previous paper Gu et al.[19a] reported that diphenyl sulfoxide is also inert to singlet oxygen; like diphenyl sulfide, if it is added to the diethyl sulfide–${}^1O_2$ reaction, it traps an intermediate to give diphenyl sulfone. The relative trapping abilities of diphenyl sulfide and diphenyl sulfoxide were reported to be 1;4.6 in methanol and 1:51 in benzene. Interestingly, Gu et al. also observed that in benzene, in contrast to the case of diphenyl sulfide, diethyl sulfide and diphenyl sulfoxide do not compete for a common intermediate and that the added diphenyl sulfoxide increases the total amount of diethyl sulfoxide formation by inhibiting the quenching step. According to their results, a modified mechanism (Scheme III) was proposed to describe the photooxidation of diethyl sulfide with added diphenyl sulfoxide in benzene. In this case, X was believed to be benzene or some other (unspecified) reductant (X) in the solution; this step was added to explain the lack of dependence of quenching on diethyl sulfide concentration.

Although a large number of experiments have been done on the diethyl sulfide–${}^1O_2$ reaction, no comprehensive mechanism has yet been advanced that explains all of the experimental results.

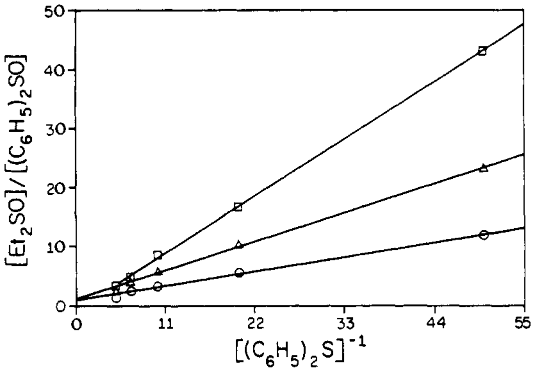


Figure 1. $(C_6H_5)_2S$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in MeOH: (○) 0.02 M Et_2S, slope = 0.224; (△) 0.05 M Et_2S, slope = 0.444; (□) 0.10 M Et_2S, slope = 0.880.

Recently, two very important studies of trapping of the intermediate by various compounds appeared. Ando et al. reported that when diaryl sulfides are used as trapping agents in methanol, they act as *nucleophiles*; i.e., the intermediate is an *electrophile*.[20] Sawaki and Ogata independently reported that sulfoxides function as *electrophiles* toward the intermediate in benzene; i.e., the intermediate is a *nucleophile* under their conditions.[21] These two observations and the previous kinetic results strongly suggested that there might be more than one intermediate involved in the diethyl sulfide–${}^1O_2$ reaction. In the present paper, a mechanism containing two intermediates for the sensitized photooxidation of diethyl sulfide is proposed that is consistent with all available experimental results.

Experimental Section

Materials. Mallinckrodt spectral grade solvents were used for the experiments in methanol, acetonitrile, and benzene. Benzene was refluxed over P_2O_5 and distilled before use. Methanol and acetonitrile were used as received. Rose Bengal (Aldrich), zinc *meso*-tetraphenylporphine (ZnTPP, Strem Chemicals Inc.), and 21*H*,23*H*-*meso*-tetraphenylporphine (*meso*-TPP, Aldrich) were used as received. Diethyl sulfide (Aldrich) was refluxed over sodium metal and distilled before use. Diphenyl sulfide (Aldrich) was distilled over calcium hydride under vacuum. Diphenyl sulfoxide (Aldrich) was recrystallized from methanol.

Methods. All photooxidations were carried out in Pyrex test tubes presaturated with oxygen. Irradiations (650-W Sylvania tungsten-halogen lamp at 50–70 V, 10% aqueous $K_2Cr_2O_7$ filter solution) were done in a merry-go-round apparatus. Rose Bengal (8×10^{-5} M) was the sensitizer in methanol and acetonitrile; ZnTPP (2×10^{-4} M) and *meso*-TPP (2×10^{-4} M) were the sensitizers in benzene. In all cases, the conversions of starting material were kept below 15%.

Yields of photooxidation products were determined by gas chromatography (HP 5720 A and HP 5880 with either a 3 ft × ${}^1/_8$ in. 3% Carbowax 20M or a 20 in. × ${}^1/_8$ in. 10% Carbowax 20M column on 100/200 mesh Chromosorb). The GC conditions were as follows: injection temperature 250 °C, detector temperature 250 °C, oven initial temperature 120 °C, oven initial time 13 min, oven program rate 8 °C/min, oven final temperature 200 °C, oven final time 20 min. Either hexamethylbenzene, diphenylmethane, or triphenylbenzene was used as internal standard.

Results and Discussion

Trapping of the Intermediate by Diphenyl Sulfide in Methanol. In Scheme I, the intermediate either reacts with the trap, diphenyl sulfide, to give diphenyl sulfoxide or with another molecule of diethyl sulfide to form diethyl sulfoxide. If Scheme I holds, steady-state eq 1 can be derived; in each expression, the concentrations on the left are those formed in a given time of irradiation. Since

$$[Et_2SO] = K\frac{2k_{SO}[Et_2S] + k_{Ph}[Ph_2S]}{k_{Ph}[Ph_2S] + K_{SO}[Et_2S]}$$

and

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$$[\mathrm{Ph_2SO}] = K\frac{k_{\mathrm{Ph}}[\mathrm{Ph_2S}]}{k_{\mathrm{Ph}}[\mathrm{Ph_2S}] + k_{\mathrm{SO}}[\mathrm{Et_2S}]}$$

therefore

$$\frac{[\mathrm{Et_2SO}]}{[\mathrm{Ph_2SO}]} = 1 + \frac{2k_{\mathrm{SO}}[\mathrm{Et_2S}]}{k_{\mathrm{Ph}}[\mathrm{Ph_2S}]} \qquad (1)$$

where K is the amount of $^1O_2$ formed in a given time.

Scheme I predicts that a plot of $[Et_2SO]/[(C_6H_5)_2SO]$ vs. $[(C_6H_5)_2S]^{-1}$ will be linear and that the slope of the lines should be dependent on the concentration of diethyl sulfide.

Photooxidation of three different concentration of diethyl sulfide in the presence of various amounts of diphenyl sulfide were carried out in methanol. Figure 1 is the plot of the results plotted according to 1. As predicted by Scheme I, the plot is linear and the slope is proportional to the concentration of diethyl sulfide. This result confirms that, in methanol, diethyl and diphenyl sulfides compete for a common intermediate, as expected by Scheme I and in good agreement with previous work of Foote and Peters.[5,6]

The average value of the ratio k_{SO}/k_{Ph}, derived from Figure 1 and eq 1, is 4.81, similar to the value reported previously by Foote and Peters ($k_{SO}/k_{Ph} = 4.0$).[5,6]

Trapping of the Intermediate by Diphenyl Sulfoxide in Methanol. Diphenyl sulfoxide is a better trap for the intermediate in the diethyl sulfide–$^1O_2$ reaction than diphenyl sulfide.[19] If the trapping of the intermediate by diphenyl sulfoxide is similar to that by diphenyl sulfide, similar kinetics (Scheme IV) to that of Scheme I should hold and eq 2 should result. Since dialkyl sulfoxides also

$$\frac{[\mathrm{Et_2SO}]}{[\mathrm{Ph_2SO_2}]} = 1 + \frac{2k_{\mathrm{SO}}[\mathrm{Et_2S}]}{k_{\mathrm{PhO}}[\mathrm{Ph_2SO}]} \qquad (2)$$

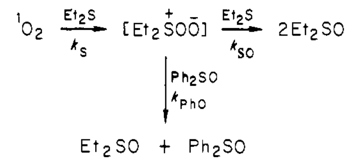
trap the intermediate,[12,19a] eq 2 holds only if the conversion of diethyl sulfide is kept low enough that trapping of the intermediate by product diethyl sulfoxide can be neglected.[22]

Figure 2 is a plot of the observed data according to eq 2 at three different concentrations of diethyl sulfide in the presence of various amounts of diphenyl sulfoxide in methanol. Again, as predicted by eq 2, the slope of the straight lines is dependent upon the concentration of diethyl sulfide. This plot also shows clearly the competitive trapping of the intermediate by diethyl sulfide and diphenyl sulfoxide, which requires a constant intercept. The average value of the ratio k_{SO}/k_{PhO} is 2.77.

Trapping of the Intermediate by Diphenyl Sulfoxide in Aprotic Solvents. As described above, the kinetic behavior predicted by Scheme IV was observed for the trapping of the intermediate in the diethyl sulfide–$^1O_2$ reaction by diphenyl sulfoxide in methanol. However, when similar experiments were carried out in aprotic solvents (benzene or acetonitrile), the results were strikingly different. Figures 3 and 4 are plots of the product ratio $[Et_2SO]/[(C_6H_5)_2SO_2]$ vs. $[(C_6H_5)_2SO]^{-1}$ at three different concentrations of diethyl sulfide for trapping of the intermediate by various concentration of diphenyl sulfoxide in benzene and acetonitrile, respectively.

As in methanol (Figure 2), these plots are straight lines. However, contrary to the results in methanol, the slopes of the lines are *independent* of diethyl sulfide concentration. This result implies that diethyl sulfide and diphenyl sulfoxide are *not* competing for a common intermediate in aprotic solvents.

Scheme IV



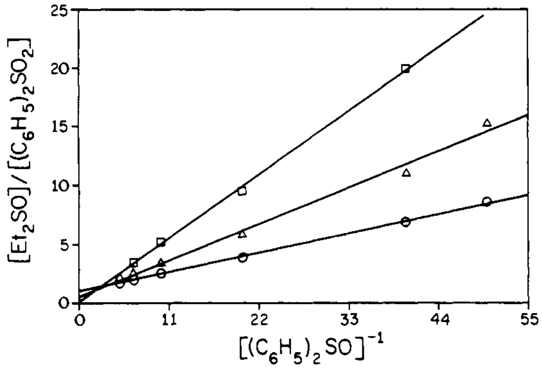


Figure 2. $(C_6H_5)_2SO$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in MeOH: (○) 0.02 M Et_2S, slope = 0.13; (△) 0.05 M Et_2S, slope = 0.26; (□) 0.10 M Et_2S, slope = 0.49.

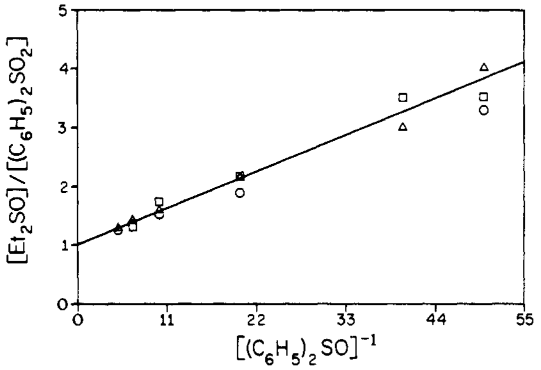


Figure 3. $(C_6H_5)_2SO$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in benzene: (○) 0.02 M Et_2S, slope = 0.046; (△) 0.05 M Et_2S, slope = 0.046; (□) 0.10 M Et_2S, slope = 0.048.

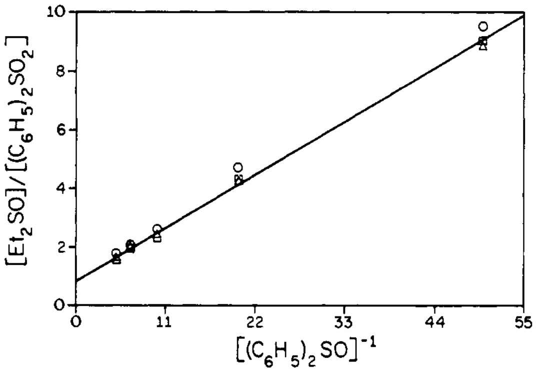


Figure 4. $(C_6H_5)_2SO$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in CH_3CN: (○) 0.02 M Et_2S, slope = 0.172; (△) 0.05 M Et_2S, slope = 0.158; (□) 0.10 M Et_2S, slope = 0.165.

Although Scheme IV describes the reaction successfully in methanol, it fails to explain the cophotooxidation of diethyl sulfide and diphenyl sulfoxide in aprotic solvents. Many different explanations for this unusual behavior have been considered. For example, Gu et al,[19] suggested that the primary intermediate can form sulfoxide without the intervention of a second sulfide molecule in aprotic solvents by a mechanism shown in Scheme III. This scheme explains well the observation that the amount of trapping depends on the concentration of the trap but not on that of diethyl sulfide; it also accounts for the lack of competition between diethyl sulfide and diphenyl sulfoxide. However, "X" was not satisfactorily described. It was thought to be benzene or another unspecified

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(22) Sulfoxides can be oxidized to sulfones but with a far lower rate compared to that of sulfides to sulfoxides.[1,18] Foote et al.[6] also reported that 0.01 M diethyl sulfoxide in dry benzene containing 1 × 10^{-4} M ZnTPP gave no sulfone after 20 min of irradiation (5 × 10^{-5} M could have been detected). In this paper, the conversion of diethyl sulfide is kept below 15%; therefore, further oxidation of diethyl sulfoxide to diethyl sulfone can be neglected.

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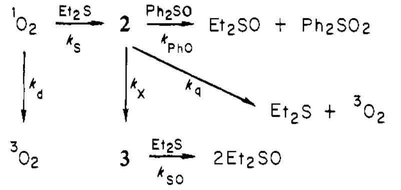
Scheme V



reductant; however, it cannot be benzene alone, because there is not enough phenol formed to account for the reduction of the intermediate.[21]

It is known that the intermediate trapped by diphenyl sulfide is electrophilic according to the results of Ando et al.[20] On the other hand, the intermediate trapped by diphenyl sulfoxide is nucleophilic from Sawaki and Ogata's results.[21] Therefore, it seems likely that not one but two intermediates are involved in the reaction.

Scheme V is the simplest mechanism that can explain the photooxidation of diethyl sulfide in the presence of added diphenyl sulfoxide in aprotic solvents, In this scheme, there is a nucleophilic intermediate, **2**, which either reacts with diphenyl sulfoxide to give diethyl sulfoxide and diphenyl sulfone (k_{Ph}), loses oxygen (k_q), or decays by a first-order process (k_X) to the electrophilic intermediate **3**, which is no longer trapped by diphenyl sulfoxide but reacts with diethyl sulfide to form diethyl sulfoxide. The structures of the intermediates that are assigned to **2** and **3** will be discussed subsequently.

In an earlier quenching study, Foote and Peters[6] observed that the quenching to oxidation ratio in aprotic solvents is independent of the sulfide concentration. In order to fit this requirement, the quenching process in Scheme V must occur at an earlier stage than the trapping of the intermediate by diethyl sulfide. In the absence of trapping agents, steady-state kinetic treatment of Scheme V would give the following forms.

$$\text{fraction of quenching} = \frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{k_q}{k_X + k_q}$$

$$\text{fraction of oxidation} = \frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{2k_X}{k_X + k_q}$$

Thus

$$\text{quenching/oxidation} = k_q/2k_X$$

The above expression predicts that the ratio of quenching to oxidation is independent of diethyl sulfide concentration, as observed.[2,6] This scheme also explains the *inhibition* of quenching by added diphenyl sulfoxide, which actually increases the amount of diethyl sulfoxide formed by this inhibition by diversion of intermediate **2** (k_{PhO}).[19a]

If steady-state kinetics are assumed in the photooxidation of diethyl sulfide with added diphenyl sulfoxide in aprotic solvents, Scheme V leads to the following relationships. Since

$$[Et_2SO] = K\frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{2k_X + k_{PhO}[Ph_2SO]}{k_X + k_q + k_{PhO}[Ph_2SO]}$$

and

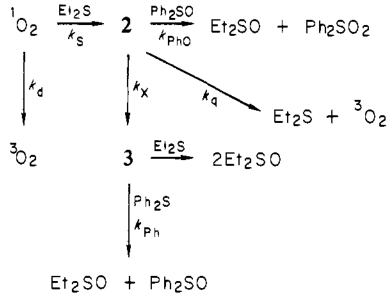
$$[Ph_2SO_2] = K\frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{k_{PhO}[Ph_2SO]}{k_X + k_q + k_{PhO}[Ph_2SO]}$$

therefore

$$\frac{[Et_2SO]}{[Ph_2SO_2]} = 1 + \frac{2k_X}{k_{PhO}[Ph_2SO]} \qquad (3)$$

The prediction of eq 3 is in excellent agreement with the observations shown in Figures 3 and 4, in which the slope of the lines in all of the plots is independent of the concentration of diethyl sulfide. The average value of ratio k_X/k_{PhO} is 0.023 M in benzene and 0.082 M in acetonitrile, These values cannot be directly compared with values calculated by Gu et al.,[19a] since a different kinetic scheme was used for the analysis of the data.

Scheme VI



From the above discussion, Scheme V can also be consistent with the results of both Ando[20] and Sawaki[21] et al. since there are two different intermediates. Intermediate **2**, which reacts with sulfoxides, must be a nucleophile, while intermediate **3**, which reacts with sulfides, must be an electrophile to be consistent with their results.

Trapping of the Intermediate by Diphenyl Sulfide in Aprotic Solvent. Although Scheme V successfully explains the photooxidation of diethyl sulfide with added diphenyl sulfoxides in aprotic solvents, a further test of its generality is necessary. Diphenyl sulfide acts as a nucleophile according to Ando's result;[21] therefore, it should trap the electrophilic intermediate (**3** in Scheme V) in aprotic solvents. This should lead to a competition between diethyl sulffide and diphenyl sulfide for the second intermediate. Scheme VI expands Scheme V to show this possibility. (See below for a discussion of structures of the intermediates.)

In Scheme VI, both diethyl and diphenyl sulfides trap the electrophilic intermediate **3**; the quenching process occurs at an earlier stage. If Scheme VI holds, in the case of the diethyl sulfide–$^1O_2$ reaction in the presence of diphenyl sulfide in aprotic solvents, steady-state kinetic eq 4 can be derived. Since

$$[Et_2SO] = K\frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{k_X}{k_q + k_X}\,\frac{k_{Ph}[Ph_2S] + 2k_{SO}[Et_2S]}{k_{Ph}[Ph_2S] + k_{SO}[Et_2S]}$$

and

$$[Ph_2SO] = K\frac{k_S[Et_2S]}{k_d + k_S[Et_2S]}\,\frac{k_X}{k_q + k_X}\,\frac{k_{Ph}[Ph_2S]}{k_{Ph}[Ph_2S] + k_{SO}[Et_2S]}$$

Therefore

$$\frac{[Et_2SO]}{[Ph_2SO]} = 1 + \frac{2k_{SO}[Et_2S]}{k_{Ph}[Ph_2S]} \qquad (4)$$

From eq 4, Scheme VI predicts that the slope of the straight lines from the plot of $[Et_2SO]/[(C_6H_5)_2SO]$ vs. $[(C_6H_5)_2S]^{-1}$ should depend upon the concentration of diethyl sulfide if diphenyl sulfide is used as the trap.

Figure 5 and 6 are plots according to eq 4 for the photooxidation of three different concentrations of diethyl sulfide in the presence of various amounts of diphenyl sulfide in benzene and acetonitrile. The kinetic behavior follows quite well that predicted by Scheme VI, including competitive trapping of the intermediate by diethyl sulfide and diphenyl sulfide. The average value of the ratio k_{SO}/k_{Ph} is 17.63 in benzene and 36.5 in acetonitrile.

These results confirm the assertion that there are two intermediates; one acts as a nucleophile (which quenches or reacts with sulfoxide) while the other functions as an electrophile and reacts with sulfides. Diethyl and diphenyl sulfide compete for **3**, but diphenyl sulfoxide acts at an earlier stage. The ratios of relative rate constants of the sensitized photooxidation of diethyl sulfide with trapping agents are summarized in Table I.

From this table, the rate of intermediate trapping by diethyl sulfide (k_{SO}) is faster than that by diphenyl sulfide (k_{Ph}) or diphenyl sulfoxide (k_{Ph}) in methanol (4.81- and 2.77-fold, respectively). The relative rate of intermediate trapping by diphenyl sulfide and diphenyl sulfoxide is 1:1.71, which is smaller than that

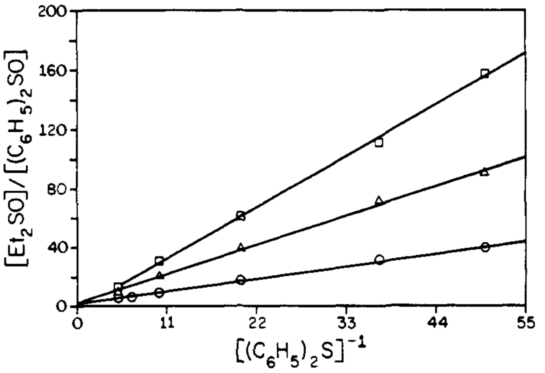


Figure 5. $(C_6H_5)_2S$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in benzene: (○) 0.02 M Et_2S, slope = 0.766; (△) 0.05 M Et_2S, slope = 1.799; (□) 0.10 M Et_2S, slope = 3.147.

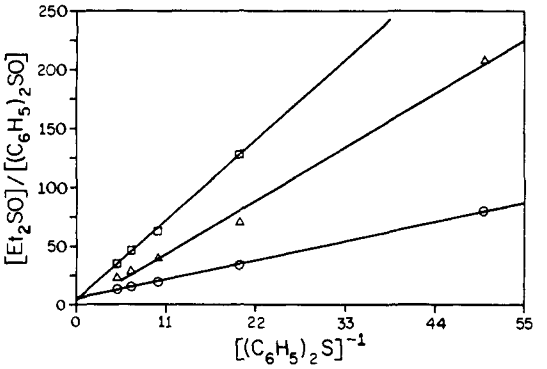


Figure 6. $(C_6H_5)_2S$ trapping of Et_2S photooxidation intermediate as a function of both concentrations in CH_3CN; (○) 0.02 M Et_2S, slope = 1.488; (△) 0.05 M Et_2S, slope = 4.125; (□) 0.10 M Et_2S, slope = 6.207.

Table I. Ratios of Relative Rate Constants (See Scheme VI)

trapping agents	ratio of rel rate	MeOH	C_6H_6	CH_3CN
$(C_6H_5)_2S$	k_{SO}/k_{Ph}	4.81 $(4.0)^a$	17,63	36.5
$(C_6H_5)_2SO$	k_{SO}/k_{PhO}	2.77		
$(C_6H_5)_2SO$	k_x/k_{PhO}		0.023 M, 0.016 M^b	0,082 M

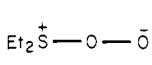
[a] See ref 5 and 6. [b] Calculated from data in ref 25.

obtained by Gu et al. (1;4,6),[19a] The difference in these values probably reflects the fact that the present value was obtained from two separate experiments, which results in some cumulative inaccuracies compared to the direct competition measurement by Gu et al.

The first row of Table I also shows that the ratio of the relative rate of intermediate trapping by diethyl sulfide to that of diphenyl sulfide (k_{SO}/k_{Ph}) is much greater in aprotic solvents than in protic solvent; the value in acetonitrile is also larger than that in benzene. (The effect of a protic solvent will be discussed in the next section,) In aprotic solvents, the relative rate of trapping of **2** by sulfoxide (k_{PhO}) to that of decay (k_X) from **2** to **3** increases in acetonitrile relative to benzene.

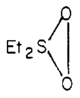
Scheme VI is also consistent with the temperature-dependence studies reported previously,[5,19b] Intermediate **2** causes the quenching at room temperature by losing oxygen. The effect of temperature can be understood if k_q has a larger temperature dependence than k_X, so that the amount of quenching decreases as the temperature is lowered; the effect is to increase the apparent rate of disappearance of sulfide, since the rate (k_S) of interaction of the sulfide with singlet oxygen is nearly independent of temperature.[19b]

Although it is clear that there are two intermediates, their structures are not certain, The structures written below are hypothetical, suggested by the reported nucleophilicity of the first and electrophilicity of the second. The persulfoxide **2** might be expected to react as a nucleophile with the electrophile sulfoxide, while the cyclic sulfurane (thiadioxirane **3**) might be expected



$\mathrm{Et_2\overset{+}{S}{-}O{-}\overset{-}{O}}$

2

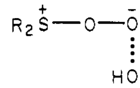


3

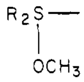
to act as an electrophile in its reaction with sulfides. An ion pair intermediate ($R_2S^+O_2^-$) is a conceivable alternative structure for **2**.

Mechanism in Methanol. The situation in methanol is quite different from that in benzene. The effect of a protic solvent on the reaction is to dramatically favor product formation at the expense of quenching, with very little effect on the rate of total singlet oxygen removal.[2,5,6,10] In addition, no matter what the trapping agent is, the slopes of all of the plots (see Figures 1 and 2) are dependent upon the amounts of diethyl sulfide; i.e., both diphenyl sulfide and diphenyl sulfoxide compete with diethyl sulfide for the intermediate.

There are at least two possibilities that can account for these observations, First, methanol may stabilize the nucleophilic intermediate **2** by hydrogen bonding[5,6] to keep it from closing to the electrophilic intermediate **3**, Hydrogen bonding would decrease the negative charge on oxygen making the intermediate more electrophilic, so that it could react with either the sulfides or sulfoxides.



$\mathrm{R_2\overset{+}{S}{-}O{-}\overset{-}{O}\cdots HOCH_3}$



$\mathrm{R_2S(OCH_3){-}OOH}$

A second possibility is that methanol actually adds to the intermediate to give a peroxysulfurane similar to those characterized by Martin et al,[11] This intermediate should have reactivity like a peracid and would be expected to react with both the sulfoxide and the sulfide, Because of the effect of solvent stabilization, the formation of the intermediate **3** is negligible, and Scheme I, which describes competitive trapping of a simple intermediate by both diphenyl sulfoxide and diphenyl sulfide with diethyl sulfide in methanol, is in satisfactory agreement with observation.

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Registry No. Diethyl sulfide, 352-93-2; diphenyl sulfoxide, 945-51-7; diphenyl sulfide, 139-66-2.