

## Effect of Protic Cosolvents on the Photooxygenation of Diethyl Sulfide

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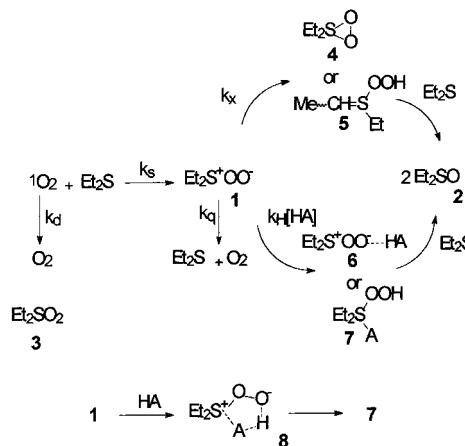
The sluggish ( $k_r < 10k_q$ ) photooxygenation of diethyl sulfide in both benzene and other aprotic solvents such as acetone and acetonitrile is made efficient by addition of small amounts of alcohols and, with a much more conspicuous increase, of phenols and carboxylic acids ( $\leq 0.1\%$  additive is sufficient in this case). A kinetic analysis shows that the effect is accounted for by interaction of the protic additives with the first formed intermediate, the persulfoxide, in competition with cleavage to the components. The thus obtained rate constants  $k_H$  linearly correlate with the acid strength of the additives, and the effect is rationalized as a general acid catalysis. Hydrogen bonding of the persulfoxide under this condition accounts in an economic way for the observed data, including co-oxygenation of  $\text{Ph}_2\text{SO}$  in mixed solvents.

The photooxygenation of sulfides continues to be a topic of mechanistic debate.<sup>1</sup> A key issue that must be addressed is why alkyl sulfides are good quenchers of singlet oxygen ( $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for diethyl sulfide,<sup>2</sup> independently from the nature of the solvent),<sup>3</sup> while the rate of chemical reaction ( $k_r$ , eq 1) is at least an order of



magnitude lower in solvents such as benzene or acetonitrile.<sup>2b,3</sup> Differently from the case of amines (which are better donors), the inefficiency is not explained on the basis of reversible charge transfer. In a seminal paper, Foote provided evidence for the mechanism in Scheme 1,<sup>4</sup> where the intermediate formed by  $^1\text{O}_2$  addition (assumed to be persulfoxide **1**) does not give directly the final products (the sulfoxide **2** with a small percentage of sulfone **3**). Rearrangement to a “second intermediate” is first required ( $k_x$  in the Scheme); this step is slow, however, and decay to the ground state ( $k_q$ ) predominates. Subsequent work from various laboratories fully supported this view.<sup>1</sup> In particular, recent calculations<sup>5,6</sup> evidenced that the persulfoxide is not stabilized with respect to the reagents and suggested that the second intermediate is ylide **5** rather than thiadioxirane **4** as

Scheme 1



previously hypothesized. From Foote’s work it was also known that the photooxidation is efficient in methanol, where a single intermediate is involved.<sup>4</sup> Clennan showed<sup>3</sup> that addition of 1.5% MeOH to benzene is sufficient to obtain a 10-fold increase of the rate of oxidation, and at less than 10% addition the theoretical value  $k_r = 2k_s$  is approached (two moles of sulfoxide are formed for every mole of singlet oxygen quenched).

The question is, in which way does the alcohol interact with the persulfoxide facilitating the reaction? Hydrogen bonding (**6**) and nucleophilic addition to form hydroperoxyalkoxysulfurane **7** ( $\text{A} = \text{OMe}$ ) were originally considered by Foote.<sup>4</sup> Later work by Clennan, particularly with intramolecular models, substantiated the latter hypothesis.<sup>7</sup> In a recent study, however, this author compared different alcohols as cosolvents in benzene and found that their effect was *not* determined by their nucleophilicity (trifluoroethanol enhanced the photooxidation rate more than nonfluorinated alcohols). On this basis, he suggested a “concerted” addition of the alcohols to **1** via an activated complex **8** (Scheme 1, lower part),<sup>3</sup> while excluding a proton-transfer mechanism.

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(1) (a) Clennan, E. L. *Sulfur Rep.* 1996, 19, 171. (b) Ando, W.; Takada, T. In *Singlet O<sub>2</sub>*; Frimer, A. A., Ed.; CRC: Boca Raton, 1985; Vol. 3, p 1. (c) Ando, W. *Sulfur Rep.* 1981, 1, 143. Foote, C. S. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press, New York, 1979; p 139. (d) Gorman, A. A. *Adv. Photochem.* 1992, 17, 217. (e) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, p 49. (f) Bellus, D. *Adv. Photochem.* 1979, 11, 105.

(2) (a) Most recently reported value, ref 2b; similar values ((2–3 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>) have been reported previously, refs 2c,d. (b) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* 1995, 117, 4218. (c) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* 1979, 29, 765. (d) Wilkinson, F. In *Singlet Oxygen. Reaction with Organic Compounds and Polymers*; Ranby, B., Rabek, J. F., Eds.; Wiley: London, 1978; p 27.

(3) Clennan, E. L.; Greer, A. *J. Org. Chem.* 1996, 61, 4793.

(4) Liang, J. J.; Gu, C. L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* 1983, 105, 4717.

(5) Jensen, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* 1998, 120, 4439.

(6) McKee, M. L. *J. Am. Chem. Soc.* 1998, 120, 3963.

(7) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* 1990, 112, 4044. Clennan, E. L.; Yang, K.; Chen, X. *J. Org. Chem.* 1991, 56, 5251. Clennan, E. L.; Yang, K. *J. Org. Chem.* 1992, 57, 4477.

## Results

In a parallel study, we found that benzyl sulfide oxygenation was affected by a variety of protic additives, not only by alcohols.<sup>8</sup> This induced us to pursue the investigation also with diethyl sulfide. We thus oxidized Et<sub>2</sub>S in the presence of zinc porphine in benzene doped with *m*-nitrophenol and acetic and chloroacetic acid, as well as with the previously tested methanol and trifluoroethanol. The reaction was in every case limited to  $\leq 10\%$  conversion. It was immediately apparent that stronger acids led to the same effect as the alcohols, i.e., an increase of the photooxidation to sulfoxide **2**, but this was reached at a much lower ( $\leq 0.01$  M) concentration of the additive. Within these limits the rate increased with the concentration of the protic additive. At a larger concentration of the present carboxylic acids or with stronger acids, e.g., trifluoroacetic acid, the rate decreased, apparently due to protonation of the sensitizing dye, as shown by the change in the color of the solution. The course of the reaction did not vary, however. The sulfoxide was in any case the main product, and the yield of sulfone **3** decreased from a few percent obtained in neat benzene to only traces in the presence of the protic additives, as it is also obtained in neat methanol. If  $k_H$  is the rate of the oxidation path induced by the additives and using Foote's formalism,<sup>4</sup> the concentration of sulfoxide formed in a given time of irradiation is as given in eq 2,

$$[\text{Et}_2\text{SO}] = K \frac{k_s[\text{Et}_2\text{S}]}{k_d + k_s[\text{Et}_2\text{S}]} \frac{2k_x + 2k_H[\text{HA}]}{k_x + k_q + k_H[\text{HA}]} \quad (2)$$

where  $K$  is the amount of  ${}^1\text{O}_2$  formed in a given time. Neither  $K$  nor  $k_d$  change significantly with the addition of the dopant within the limits explored, as it was shown by parallel actinometric experiments where the photo-oxidation of octaline was measured to occur at unchanged rate in the same solvent mixtures. This was expected, since Clennan<sup>3</sup> demonstrated that both  $k_s$  and  $k_d$  change within 10% by addition of MeOH to benzene up to 1.85 M, and a fortiori no significant effect should occur with the small amounts of additives we used.<sup>9</sup> Therefore, eq 2 can be simplified to eq 3, where  $K'$  is constant for the whole series of experiments (in the reciprocal form, eq 4).

Furthermore, the increase in the formation of the sulfoxide with respect to neat benzene was large (by a factor of 5 to  $> 15$ ) in all experiments except at very low additive concentration. Under these boundary conditions,  $k_x \ll k_H[\text{HA}]$  and eq 4 simplifies to eq 5.

$$[\text{Et}_2\text{SO}] = K' \frac{2k_x + 2k_H[\text{HA}]}{k_x + k_q + k_H[\text{HA}]} \quad (3)$$

$$[\text{Et}_2\text{SO}]^{-1} = (1/K') \frac{k_x + k_q + k_H[\text{HA}]}{2k_x + 2k_H[\text{HA}]} \quad (4)$$

$$\cong (1/2K')(1 + (k_q/k_H)[\text{HA}])^{-1} \quad (5)$$

This predicts that doubly reciprocal plots of the yield of Et<sub>2</sub>SO in a given time vs the acid concentration are

(8) Bonesi, S. M.; Mella, M.; d'Alessandro, N.; Aloisi, G. G.; Vanossi, M.; Albini, A. *J. Org. Chem.* **1998**, *63*, 9946.

(9) At any rate, the ratio  $k_s[\text{Et}_2\text{S}]/k_d$  is close to 1 (ca. 96%) in these experiments; thus  $K \cong K'$ .

linear and have the same intercept. This is what is actually observed, as shown in Figure 1a. The intercept vs slope ratio is  $k_H/k_q$ , and the values thus obtained are reported in Table 1.

As mentioned above, Foote reported that the photo-oxidation of sulfides is inefficient also in a polar aprotic solvent such as acetonitrile. We thus explored the effect of the same protic additives as well as water also in this solvent (in this case the sensitizer was Rose Bengal) and observed again a large increase in the rate of sulfoxide formation. The effect was slightly smaller than in benzene, but with a similar dependence on the acid strength. Linear [Et<sub>2</sub>SO] vs [HA] reciprocal plots were again obtained (see Figure 1b,c and Table 1 for the values of  $k_H/k_q$ ).

Finally, we carried out a similar study in acetone. This extension was prompted by the fact that Clennan reported a peculiar effect upon the photooxidation of diethyl sulfide in acetone-methanol mixtures at  $-80^\circ\text{C}$ .<sup>10</sup> Under this condition and carrying out the reaction at 100% Et<sub>2</sub>S conversion, he observed an anomalous increase of the sulfone formation; namely, the Et<sub>2</sub>SO<sub>2</sub>/Et<sub>2</sub>SO ratio was 0.23 in neat acetone but grew to 2.2 in the presence of 5% MeOH, while dropping again at a larger MeOH content. We were curious to see whether such an effect would show up also under our conditions. However, at room temperature and low conversion our results essentially replicated those obtained in benzene and acetonitrile, although the amount of protic dopant required for observing the same effect was somewhat larger. Once again, the effect was only a large increase in the rate of formation of the sulfoxide, with a decrease, not an increase, in the proportion of sulfone, and linear reciprocal plots were obtained. The  $k_H/k_q$  values were estimated as in the previous cases (as shown in Figure 1d,e and Table 1).

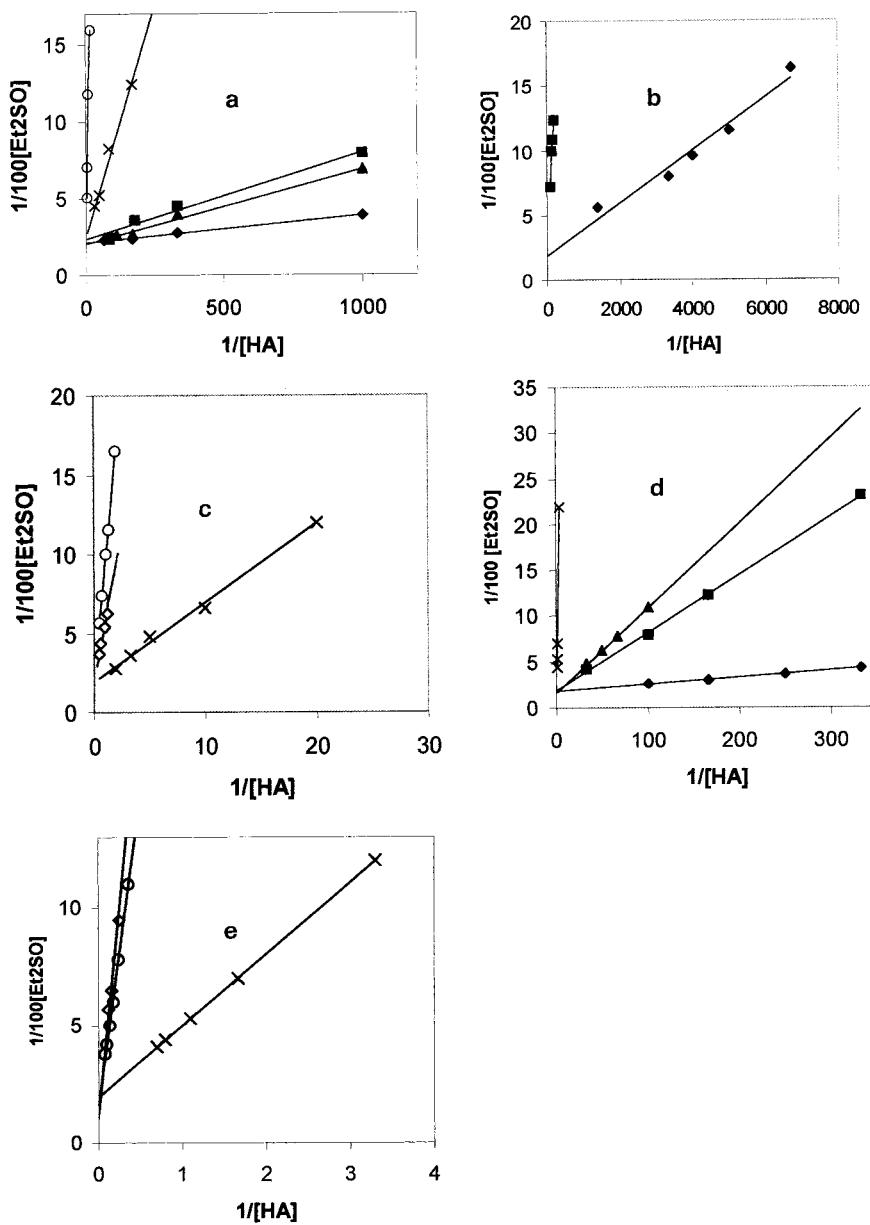
The  $k_H/k_q$  values obtained in the three solvents all showed a similar dependence on the acid strength of the protic additives. The logarithmic correlation of such values with gas-phase acidities ( $\Delta G^\circ$ ) is shown in Figure 2. Gas-phase values<sup>11</sup> were used because they are likely to better match the situation in aprotic solvents than would the acidities in water.

A further characterization of the intermediate involved in the reaction in mixed solvents was obtained through the study of diphenyl sulfoxide co-oxygenation. It is known that Ph<sub>2</sub>SO, while being insensitive to singlet oxygen, is co-oxidized to Ph<sub>2</sub>SO<sub>2</sub> when photooxygenated in the presence of Et<sub>2</sub>S. Foote showed that the ratio [Et<sub>2</sub>SO]/[Ph<sub>2</sub>SO<sub>2</sub>] is linearly dependent on [Ph<sub>2</sub>SO]<sup>-1</sup> both in MeOH and in benzene.<sup>4</sup> We carried out a similar study on the diethyl sulfide oxidation in benzene containing 0.05 M AcOH and found again a linear behavior, with a slope of 0.16 (Figure 3). This is closer to the slope measured in neat methanol than to that in neat benzene.

## Discussion

The above data fit nicely in the generally accepted photooxidation mechanism (Scheme 1) and allow a better

(10) (a) Clennan, E. L.; Yang, K. *Tetrahedron Lett.* **1993**, *34*, 1697. (b) with other sulfides, such a complex dependence on methanol addition at low temperature is observed also in toluene; see also: Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218–4227. (11) (a) Cummings, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1. (b) Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1981**, *103*, 4017. (c) Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6056.



**Figure 1.** Doubly reciprocal plot for the yield of diethyl sulfoxide (M) vs the concentration of the protic additive (M): (a) in benzene; (b, c) in acetonitrile; (d, e) in acetone. Additives: chloroacetic acid ( $\blacklozenge$ ), acetic acid ( $\blacksquare$ ), *m*-nitrophenol ( $\blacktriangle$ ), trifluoroethanol ( $\times$ ), methanol ( $\circ$ ), and water ( $\diamond$ ).

**Table 1. Effect of Protic Additives on the Photooxygenation of Diethyl Sulfide**

| additive         | $k_H/k_q, M^a$    |                   |                   |
|------------------|-------------------|-------------------|-------------------|
|                  | in benzene        | in acetone        | in acetonitrile   |
| $CH_2ClCOOH$     | $1.2 \times 10^3$ | $2.5 \times 10^2$ | $9.5 \times 10^2$ |
| $CH_3COOH$       | $4.2 \times 10^2$ | 26                | 39                |
| $m-O_2NC_6H_4OH$ | $4.1 \times 10^2$ | 18                |                   |
| $CF_3CH_2OH$     | 43                | 0.65              | 3.8               |
| $CH_3OH$         | $3.6^b$           | 0.03              | 0.3               |
| $H_2O$           |                   | 0.06              | 0.6               |

<sup>a</sup> As obtained from the plots in Figure 1. <sup>b</sup> By plotting in the same way as above the relative rate data ( $k_H(k_{H,rel})$ ) reported by Clennan in ref 3 (which are obtained through a different treatment of the data and at a higher MeOH concentration), the value 2.3 M is obtained.

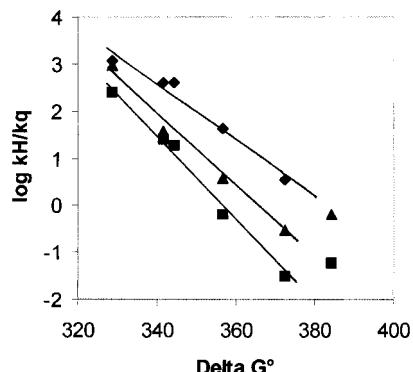
definition of the structure of the intermediates considered. The main points are indicated in the following.

Persulfoxide is not an exceedingly short-lived intermediate. Quenching by protic agents ( $k_H/k_q = 1.2 \times 10^3$

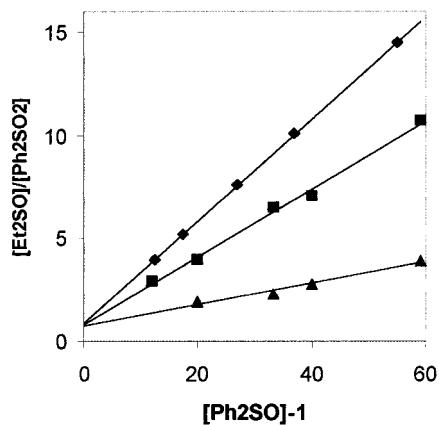
M with chloroacetic acid in benzene) requires that the lifetime of persulfoxide 1 is  $\geq 10^{-7}$  s. On the other hand, the known fact that this species is trapped by a nucleophile such as diphenylsulfoxide at a concentration as low as 0.05 M<sup>1,4</sup> also implies that it is reasonably long-lived. That fact that no spectroscopic detection of this intermediate has been reported as yet must be due to the unfavorable spectral characteristics rather than to the short lifetime.

The oxidation promoted by protic agents clearly involves general acid catalysis.<sup>12</sup> As shown in Figure 2, the ratio  $k_H/k_q$  correlates with the acidity, with an approximate linear logarithmic dependence on the acid

(12) (a) This is then another case of general acid catalysis in a photochemical reaction, being due, as in most of the other known examples (refs 12b,c), not to a direct interaction of the acid with an excited state (here singlet oxygen) but rather to the reactivity of a following intermediate (here the persulfoxide). (b) Albini, A. *J. Chem. Ed.* **1986**, *63*, 383. (c) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285.



**Figure 2.** Dependence of the  $k_H/k_d$  ratio as obtained from Figure 1 for the photooxygenation of diethyl sulfide in benzene (◆), in acetonitrile (▲), and in acetone (■) vs the acidity of the additive in the gas phase,  $\Delta G^\circ$ , kcal/mol.<sup>11</sup> Regression lines are drawn through the points, excluding water, which deviates upwards. The slopes are  $-0.06$ ,  $-0.078$  (or  $-0.06$  including water), and  $-0.093$  ( $-0.073$  including water) mol/kcal, respectively.

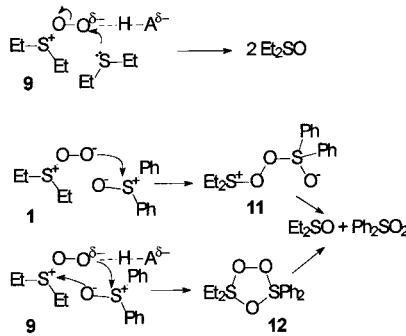


**Figure 3.** Co-oxygenation of diphenyl sulfoxide by sensitized irradiation of 0.05 M diethyl sulfide in 0.05 M AcOH (■), slope 0.166 M, intercept 0.79,  $r$  0.99; in neat benzene (▲), slope 0.053 M (ref 4, 0.046), intercept 0.72,  $r$  0.98; in neat methanol (◆), slope 0.25 M (ref 4, 0.26), intercept 0.90,  $r$  0.99.

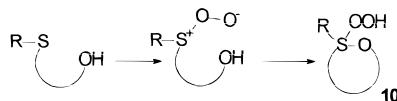
strength. Since there is no reason to expect that the rate of the collapse of the persulfoxide to the components ( $k_d$ ) is significantly affected in the presence of such small amounts of cosolvents, this is a Bronsted plot, apart from an additive constant. As it appears in Figure 2, the range of observed  $k_H$  values spans over ca. 3 orders of magnitude for a change of 70 kcal/mol in the  $\Delta G^\circ$  scale (15  $pK_a$  units). The dependence on the acidity scale is similar for the three solvents (similar slopes, see Figure 2), but the values of  $k_H$  somewhat decrease in the sequence benzene  $>$  acetonitrile  $>$  acetone. Thus, it appears that the bulk polarity of the medium (determined by the choice of the solvent, not by the amount of protic additives) has little effect on the rate, while the interaction of the key intermediate with the acid is limited to some degree by the competition with a basic solvent,<sup>13a</sup> in accord with the observed order. The values for water deviate upwards, probably because the gas-phase acidity is not well suited in this case.

(13) (a) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877. (b) We thank a reviewer for pointing out this fact.

**Scheme 2**



**Scheme 3**



An economic rationalization for the acid catalysis, and in our opinion also the most likely one, is that formation of a hydrogen bond with the persulfoxide is involved. This was one of the original hypotheses by Foote<sup>4</sup> and seems perfectly viable, even if it has been later contended that if hydrogen bonding is involved, then it should occur at a diffusion-controlled rate.<sup>3</sup> We would like to point out, first, that persulfoxides are mesomeric, rather than localized, zwitterions, although recent calculations do show that a considerable portion of the negative charge resides on the outer oxygen.<sup>5,6</sup> Second, the plots in Figure 2 show an unusually small slope ( $\alpha$  in the Brønsted equation), and this is consistent with hydrogen bonding being a reversible equilibrium process, without needing to postulate that this occurs at a rate slower than  $k_{\text{diff}}$ .<sup>13b</sup> The hydrogen-bonded persulfoxide is in fast equilibrium with the solvent–proton donor complex, and the equilibrium is shifted in progressing from a weak acid such as an alcohol to chloroacetic acid.

As far as the reactivity is concerned, Clennan pointed out<sup>7</sup> that both of the mechanisms originally proposed by Foote for the rationalization of the effect of alcohols, viz., hydrogen bonding (see formula 9 in Scheme 2) or alcohol addition to form the hydroperoxyalkoxysulfurane 7 (see Scheme 1), account for electrophilic oxygen transfer to Et<sub>2</sub>S (as well as to Ph<sub>2</sub>S).<sup>4</sup> In fact, both in 9 and in 7 the negative charge on the outer oxygen of the persulfoxide is moderated or eliminated. Clennan has supplied several pieces of evidence supporting the role of sulfurane 7, and these are compelling for the intramolecular case, where the hydroxy group is tethered to the sulfide by an alkyl chain (see formula 10 in Scheme 3).<sup>7,14</sup> However, these models do not necessarily mimic intermolecular trapping, and furthermore recent calculations failed to determine how MeOH stabilizes the persulfoxide.<sup>5</sup> In our opinion invoking concerted addition for explaining the activation by protic additives is not necessarily a general rationalization, although formation of adduct 7 may follow hydrogen bonding with reasonably nucleophilic species such as methanol.<sup>15</sup>

(14) Clennan, E. L.; Yang, K. *J. Org. Chem.* **1992**, *57*, 4477–4487.

(15) In view of the above mentioned Clennan experiments at low temperature,<sup>10</sup> a hypothesis would be that, besides that in the intramolecular case, adduct 7 is important at low temperature, where, however, the reaction course changes and, differently from what is consistently observed at room temperature, the sulfone becomes a main product. Work on this point is in progress.

On the other hand, hydrogen bonding of the persulfoxide is also compatible with maintaining the reactivity with diphenyl sulfoxide, as indicated by previous work<sup>4</sup> and confirmed here (see Figure 3).<sup>16</sup> Oxygen transfer from persulfoxide **1** to Ph<sub>2</sub>SO in *aprotic* media involves an attack of the nucleophilic outer oxygen of **1** onto the positively charged sulfur atom in the sulfoxide. This is assumed to involve an "open sulfurane" **11**, rather than cyclic intermediate **12** (see Scheme 2), as supported by labeling experiments in the presence of (CD<sub>3</sub>)<sub>2</sub>SO in aprotic solvents.<sup>17,18</sup> However, the positive charge on the sulfur atom is increased in hydrogen-bonded persulfoxide **9**, and this makes it open to attack by the sulfoxide oxygen, as shown in Scheme 2. Thus co-oxygenation of Ph<sub>2</sub>SO in the presence of protic additives or in protic solvents may proceed over **12**. This is a mechanistic alternative to the role of adduct **7**, since it is not apparent why the latter should react efficiently with Ph<sub>2</sub>SO.<sup>19</sup> At any rate, Figure 3 shows that the intermediate formed in AcOH-doped benzene parallels the chemistry of the intermediate in neat MeOH also in the reaction with sulfoxides, consistently with the proposal that interaction with acids of different strength leads in every case to the same intermediate, at least within the limits explored.<sup>20</sup>

Another possibility that has been considered is that the acids catalyze a keto-enol type equilibrium between the persulfoxide and ylide **5** (see Scheme 1) and that the latter is the actual oxidizing species. This contrasts with the fact that no deuterium exchange has been found in the photooxidation of *d*<sub>6</sub>-dimethyl sulfide or of  $\alpha$ -*d*<sub>2</sub> benzyl ethyl sulfide to the corresponding sulfoxides.<sup>8,21</sup> However, Clennan has suggested, on the basis of a study on 1,3-

(16) Comparing the rate of reaction with diphenylsulfoxide in protic ( $k_{\text{PhOH}}$ ) vs aprotic media ( $k_{\text{PhOH}}$ ) is not immediate. The ratio  $[\text{Et}_2\text{SO}] / [\text{Ph}_2\text{SO}_2]$  is linearly dependent on  $[\text{Ph}_2\text{SO}]$  in both cases, ref 4, but the slope of the straight line has a different physical meaning in MeOH, where it changes with the starting sulfide concentration (eq 5, adapted from ref 4 to the present scheme, slope =  $2k_{\text{H}}[\text{HA}][\text{Et}_2\text{S}] / k_{\text{PhOH}}$ ) and in benzene, where it is independent from it (eq 6, slope =  $2k_{\text{x}} / k_{\text{PhOH}}$ ). It is assumed that the persulfoxide is trapped in the latter case, the hydrogen bonded form in the former one.

$$\frac{[\text{Et}_2\text{SO}]}{[\text{Ph}_2\text{SO}_2]} = \frac{2k_{\text{H}}[\text{HA}][\text{Et}_2\text{S}]}{k_{\text{PhOH}}[\text{Ph}_2\text{SO}]} \quad (5)$$

$$\frac{[\text{Et}_2\text{SO}]}{[\text{Ph}_2\text{SO}_2]} = \frac{2k_{\text{x}}}{k_{\text{PhOH}}[\text{Ph}_2\text{SO}]} \quad (6)$$

(17) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203.

(18) There is some indication that cyclic intermediate **11** is involved in the case of benzyl sulfides; see ref 8.

(19) The sulfur atom has an available electron pair in sulfurane **7**, which has a trigonal bipyramidal structure (ref 5), and one may write a mechanism similar to that considered here for the hydrogen-bonded persulfoxide.

(20) It has also been suggested that methanol may act primarily as proton source at low concentration (e.g., facilitating rearrangement of **1** to **5**) and adds to **1** at a large concentration, refs 5 and 10a. The present study affords no evidence for such a double role.

(21) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, 118, 7285.

dithianes, that this is due to the hydrogen-bonded nature of the ylide,<sup>22</sup> and there is some computational hint for such a role of **5**.<sup>5</sup> At the moment, it appears safe to regard the ylide as an intermediate in the formation of the sulfone<sup>5,6,21</sup> and, in the presence of a stabilizing group in  $\alpha$ , in C–S oxidative cleavage,<sup>5,6,8,21,23</sup> but it may have a role also in the formation of the sulfoxide.

Summing up, general acid catalysis operates on the photooxygenation of diethyl sulfide, reasonably through the hydrogen-bonded persulfoxide. It appears possible that this is the single intermediate revealed by Foote in the oxidation of sulfides in MeOH. This hypothesis rationalizes the observed reaction with both sulfides and sulfoxides as well as the suppression of chemically unproductive decay to the components. The fact that an efficient oxygenation can be accomplished in aprotic solvents doped with small amounts (0.1% or less) of acids rather than in neat protic solvents may be advantageous by making the method more flexible.

## Experimental Section

**Materials.** Diethyl sulfide and diphenyl sulfoxide were commercial products. The latter was purified by chromatography and recrystallization. Diethyl sulfoxide and sulfone were prepared from the sulfide by dihydrogen peroxide and peracetic acid oxidation, respectively.<sup>24</sup> Spectroscopic grade solvents were used. Benzene and acetonitrile were freshly distilled from calcium hydride, and acetone was treated with anhydrous potassium carbonate and fractionated under dry argon. The solvents were directly distilled into the graded flasks and kept over molecular sieves.

**Photoreactions.** The photooxidations were carried out using 0.05 M solutions of diethyl sulfide in the presence of tetraphenylporphine (in benzene) or of Rose Bengal (in acetone or acetonitrile). The solutions were contained in rubber-stoppered Pyrex tubes. These were exposed to four phosphor-coated 15 W lamps (Applied Photophysics) emitting from 350 to 700 nm while a stream of dry oxygen saturated with benzene was passed in the solution through a needle.

The products were determined by GC on the basis of calibration curves in the presence of dodecane as the internal standard. An Innowax column (30 m  $\times$  0.25 mm, 0.5  $\mu\text{m}$  film thickness) was used, with He as the carrier gas. The injector pressure was constant (12 psi).

The photooxidation of octaline was carried out in parallel experiments in the same mixed solvents and likewise monitored by GC after treatment with triphenylphosphine.

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(22) Toulchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, 64, 5620.

(23) (a) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, 113, 2696. (b) Takata, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, 25, 4767. (c) Takata, T.; Ishibashi, K.; Ando, W. *Tetrahedron Lett.* **1985**, 26, 4609.

(24) Cumper, W. W. N.; Reed, J. F.; Vogel, A. I. *J. Chem. Soc.* **1965**, 5323.