Effect of Alcohols on the Photooxidative Behavior of Diethyl Sulfide

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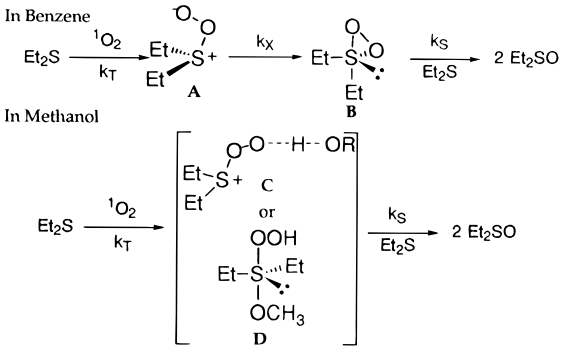
The reactions of singlet oxygen with diethyl sulfide (Et_2S) in benzene alcohol mixtures have been examined. The salient discoveries include: (1) the rate constants of product formation, k_r, in benzene/methanol mixtures are a function of the concentration of methanol, (2) the ability of alcohols to supress physical quenching are a function of their pK_a's, and (3) trapping experiments with diphenyl sulfoxide are consistent with two distinct intermediates. A mechanism which involves formation of a persulfoxide followed by reaction with methanol to give a hydroperoxy-methoxy sulfurane is consistent with all of the results.

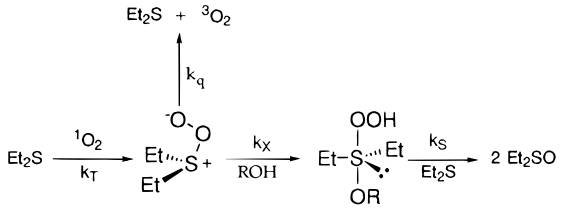
In 1983 Foote and co-workers[1] reported a study of the photooxidation of Et_2S in both benzene and methanol. The reaction exhibited remarkably different characteristics in the two solvents. In benzene two intermediates, the persulfoxide, **A**, and the thiadioxirane, **B**, were invoked to rationalize the experimental results (Scheme 1). In methanol, however, only a single intermediate was kinetically required, and speculation was provided which suggested that it was either a hydrogen-bonded persulfoxide, **C**, or a hydroperoxy sulfurane, **D**.

We report here a detailed kinetic study of this reaction in alcohol/benzene mixtures. These studies provide the first direct evidence for at least two intermediates in the presence of methanol and implicates the mechanism shown in Scheme 2. In addition, these results also demonstrate that it is the hydrogen donating ability (pK_a) of the alcohol (ROH) which most accurately predicts its ability to competitively inhibit physical quenching, k_q.

Scheme 1



Scheme 2



Results

Oxygen saturated benzene solutions containing 2×10^{-4} M TPP (tetraphenyl porphyrin) as the sensitizer, 6×10^{-4} M biphenyl as the internal standard, and 0.10 M Et_2S were irradiated with a 450 W Hanovia lamp through a 12 M $NaNO_2$ filter solution[2] and the product ratios measured by capillary column gas chromatography. At less than 15% conversion, the sulfoxide was the major product of the reactions in all cases. The sulfone decreased from a high of nearly 22% of the reaction mixture in pure benzene to a low of 1.3% in 85% methanol.[3]

The rate constants for Et_2S-induced disappearance of $^1O_2$, k_T, were measured as described previously by monitoring the quenching of the time-resolved emission of singlet oxygen at 1270 nm.[4,5] The results depicted in Table 1 indicate that these rate constants are insensitive or only slightly sensitive to increasing concentrations of methanol. The lifetime of $^1O_2$, on the other hand, does decrease with increasing concentrations of methanol as expected to give an extrapolated lifetime of 9.3 μs in pure methanol, in excellent agreement with the published value of 10.4 μs.[6]

Table 1. k_T Measurements for the Reactions of Et_2S in Benzene/Methanol Mixtures

[MeOH], M	$k_T \times 10^{-7}$ M^{-1} s^{-1}	τ, μs[a]
0	3.04 ± 0.52	23
0.25	2.70	22.26
0.62	3.12	21.95
1.23	3.41	21.57
1.85	3.35	20.53

[a] Lifetime of singlet oxygen.

The experimental results which provided the input for construction of the mechanistic proposal depicted in Scheme 2 include (1) the rates of product formation, k_r, as a function of methanol concentration in benzene, (2) the kinetic behavior of the photooxidations of Et_2S in the presence of structurally diverse alcohols, and (3) trapping experiments with diphenyl sulfoxide (Ph_2SO) in benzene/methanol mixtures.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717−4721.

(2) Parker, C. A. *Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry*; Elsevier, Inc.: New York, 1968.

(3) In benzene enhanced sulfone formation at low methanol concentration was not observed. Clennan, E. L.; Yang, K. *Tetrahedron Lett.* **1993**, *34*, 1697−1700.

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

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

(6) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201−6205.

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Table 2. Chemical Rate Constant (k_r) Measurements in Benzene/Methanol Mixtures[a,b]

[MeOH], M	$k_r \times 10^{-7}$, M^{-1} s^{-1}	[MeOH], M	$k_r \times 10^{-7}$, M^{-1} s^{-1}
0	0.385	0.81	4.84
0.37	3.35	1.23	5.21
0.42	3.36	1.84	5.60
0.61	4.22		

[a] $[Et_2S] = 0.1$ M. [b] Irradiations done on a merry-go-round and analyzed by GC using biphenyl as an internal standard.

***k_r* Measurements**. The rate constants for the chemical reactions of Et_2S with singlet oxygen, k_r, in various benzene/methanol solutions were measured in competition with adamantylideneadamantane (AdAd; $k_r = 3.49 \times 10^5$ M^{-1} s^{-1}) using the kinetic method of Higgins, Foote, and Cheng.[7] These values along with the value of k_r in pure benzene are given in Table 2. The chemical rate constants, k_r, increase by 1 order of magnitude upon addition of as little as 1.5% methanol (0.368 M) to benzene. We suggest that this remarkable rate enhancement is a result of a new mechanism in the presence of methanol which circumvents the energetically costly interconversion of the persulfoxide, **A**, to the thiadioxirane, **B**.[8−10]

Within the framework of the mechanism in Scheme 2 the slow increase in k_r as the concentration of methanol is increased from 0.3 to over 1.8 M (Table 2) can be attributed to competitive inhibition of physical quenching by rapid trapping of the persulfoxide. In benzene 94% of the interactions of Et_2S with singlet oxygen lead to physical quenching (% physical quenching $= 100 \times (k_T - 0.5k_r)/k_T$),[11] while in 1.84 M methanol only 16% physical quenching occurs. In addition to competitive inhibition of physical quenching, trapping with methanol also produces the second intermediate, the hydroperoxy sulfurane. Evidence for this additional intermediate includes the fact that Foote and co-workers[1] inferred an intermediate from kinetic studies in pure methanol which cannot be the persulfoxide since it did not regenerate triplet oxygen in a physical quenching process.

The mechanism in Scheme 2 also predicts that the rate of product formation is given by eq 1. Methanol is not consumed in this reaction, and very little is tied up at any given time in the hydroperoxy-methoxy sulfurane, and consequently k_r is essentially constant and the $1/k_r$ values should be linear when plotted versus 1/[MeOH] as predicted by eq 1a and as demonstrated by the plot shown in Figure 1. The value of k_T derived from the intercept of the plot (3.56×10^7 M^{-1} s^{-1}), which should be k_T at a hypothetical infinite concentration of methanol, is remarkably close to that measured in pure benzene ($3.04 \pm (0.52) \times 10^7$ M^{-1} s^{-1}) and reinforces our earlier conclusion that k_T is solvent independent.

Photooxidation in the Presence of Other Alcohols. The k_r's and k_T's for the photooxidations of Et_2S in benzene doped with a variety of alcohols at 0.6138 M have also been measured using the same techniques described above for the benzene/methanol mixtures. The k_r's were determined relative to octalin which required reduction of the hydroperoxide product with Ph_3P prior to GC analysis. Control reactions demonstrated that Et_2S did not react with the vinyl hydroperoxide under the reaction conditions. The k_r and k_T data from these analyses are shown in Table 3. In addition, the relative rate constants for the reactions of diethyl persulfoxide with the alcohols, k_X(rel) (Scheme 2) were calculated from these data using eq 2 and are also included in Table 3 (see Appendix I for the derivation of eq 2).

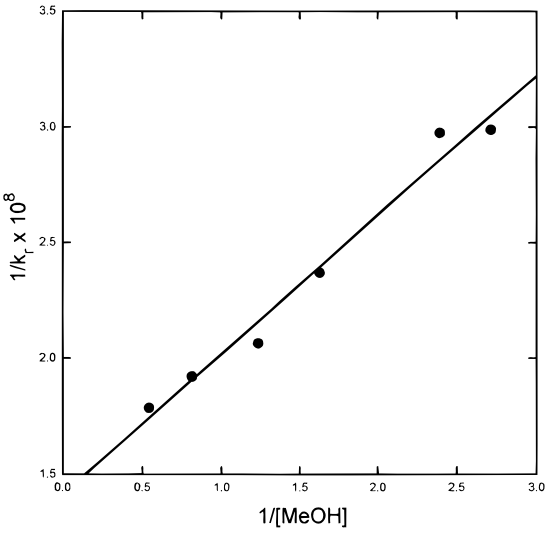


Figure 1. $(k_r)^{-1}$ versus $[MeOH]^{-1}$; slope = 0.60; intercept = 1.41; $r = 0.989611$.

Table 3. Rate Constants for Chemical Reactions of Et2S in Alcohol Solvents[a]

alcohol	$k_T \times 10^{-7}$ (M^{-1} s^{-1})	$k_r \times 10^{-7}$ (M^{-1} s^{-1})[b]	%PQ	k_X(rel)[c]
MeOH	3.12	4.05 ± 0.49[d]	35 ± 8	1.0
EtOH	2.95	2.75	53	0.47
iPrOH	2.85	1.94	66	0.28
iBuOH	2.66	1.50	72	0.21
tBuOH	2.74	0.98 ± 0.08	82 ± 2	0.12
CF_3CH_2OH	1.83	3.56 ± 0.61	3	19

[a] In benzene doped with 0.6138 M alcohol. [b] Using octalin ($k_r = 1.84 \times 10^6$ M^{-1} s^{-1}) as the reaction partner. [c] Relative k_x values calculated using eq 2. [d] Average of three values: one determined using adamanylideneadamantane ($k_r = 3.49 \times 105$ M^{-1} s^{-1}) as the reaction partner.

$$\frac{d[Et_2SO]}{dt} = \frac{2k_X k_T[Et_2S][MeOH][^1O_2]}{k_q + k_X[MeOH]} = k_r[Et_2S][^1O_2] \quad (1)$$

$$\frac{1}{k_r} = \frac{1}{2k_T} + \frac{k_q}{2k_X k_T[MeOH]} \quad (1a)$$

$$\frac{k_{X(ROH)}}{k_{X(R'OH)}} = \frac{k_{r(ROH)}}{k_{r(R'OH)}} \times \frac{(2k_{T(R'OH)} - k_{r(R'OH)})}{(2k_{T(ROH)} - k_{r(ROH)})} \quad (2)$$

The decrease in the size of k_X in the series MeOH > EtOH > iPrOH > iBuOH > tBuOH on the surface suggests that the alcohols encounter steric interactions

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

(8) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 2368−2375.

(9) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478−6487.

(10) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, pp 1−48.

(11) This equation represents an approximation since $k_T = k_q' + 0.5k_r$, where k_q' is the rate constant for physical quenching (not the microscopic rate constant k_q in Scheme 2) and k_r is the rate constant for chemical deactivation of singlet oxygen, is only valid when every molecule of singlet oxygen that chemically reacts generates two molecules of product.

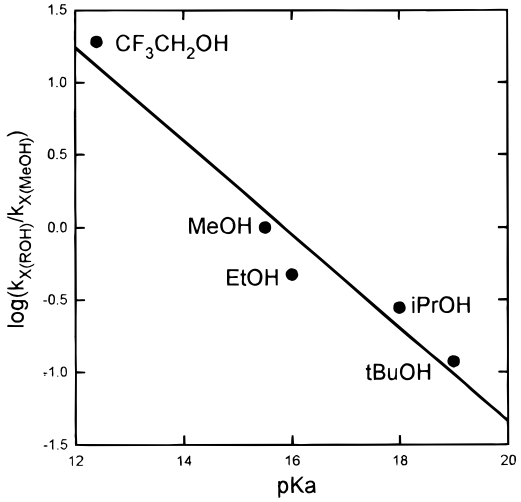


Figure 2. log of $k_{X(rel)}$ versus the pK_a of the alcohol. slope = −0.32; r = −0.997437.

in their approach to the sulfonium-ion like sulfur in the persulfoxide and that this interaction dictates the magnitude of k_X. In addition, a plot of log(k_X(rel)) versus the Taft steric parameter[12] is linear and steric interactions between apical alkoxy groups are known to decrease the yield of σ-dialkoxytriphenylphosphoranes.[13] However, this analysis does not correctly predict k_X(rel) for 2,2,2-trifluoroethanol (CF_3CH_2OH) when the Taft parameter for the sterically similar CH_3CH_2OH is used. The much reduced nucleophilicity of CF_3CH_2OH in comparison to the other alcohols does not provide a satisfactory rationale for this behavior since k_X(rel) should decrease with decreasing nucleophilicity not increase as experimentally observed.

The data is most reasonably rationalized by suggesting that it is the hydrogen donating ability of the alcohols and not the steric interaction with the approaching alkoxide which dictates the magnitude of k_X. In support of this suggestion is the observation that a plot of the pK_a's of the alcohols[14] versus log k_X(rel) is linear even when the reasonably acidic alcohol CF_3CH_2OH (pK_a = 12.4) is included (Figure 2).

Ph_2SO Trapping. We anticipated that Ph_2SO would trap both intermediates in benzene/methanol mixtures since the persulfoxide and the hydroperoxy sulfurane are successfully trapped in benzene and in methanol, respectively. Consistent with this expectation the ratio [Et_2SO]/[Ph_2SO_2] decreased with increasing concentrations of Ph_2SO. In addition, plots of this ratio versus 1/[Ph_2SO] at various high concentrations (≥20% methanol) of methanol were linear as reported in Table 4.

These observations are consistent with the trapping events as depicted in Scheme 3 in which Ph_2SO reacts with both intermediates. It can be shown within the confines of this trapping mechanism that [Et_2SO]/[Ph_2SO_2] is given by eq 3. However, at the high methanol concentrations used in this study k_X[MeOH] is large enough to completely suppress physical quenching, k_q (Scheme 3), and consequently k_{PhO}[Ph_2SO] ≪ k_X[MeOH] so that eq 3 can be approximately written as eq 3a which

Table 4. Slopes[a] of the Ph_2SO Trapping Experiments as a Function of the Concentrations of both Et_2S and MeOH

[Et_2S], M	[MeOH], M	slope
0.1	4.94	0.0547
0.1	14.81	0.118
0.1	24.69	0.49[b]
0.02	14.81	0.0345
0.05	14.81	0.0727

[a] Slopes of plots of [Et_2SO]/[Ph_2SO_2] versus [Ph_2SO]$^{-1}$ at various concentrations of Et_2S and MeOH. [b] Reference 1.

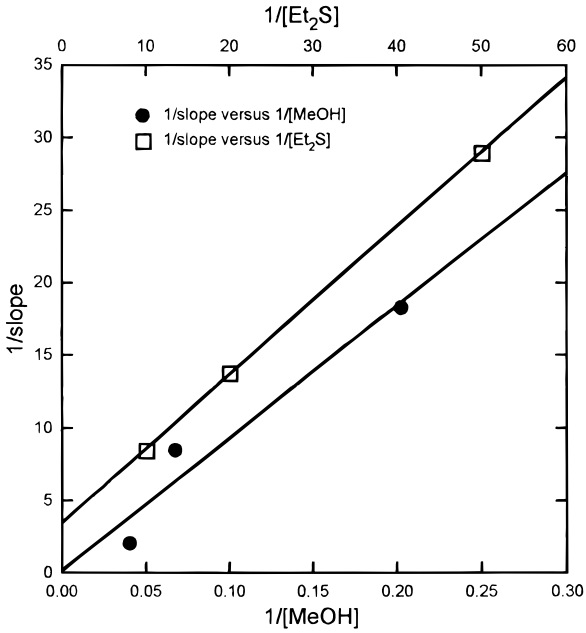
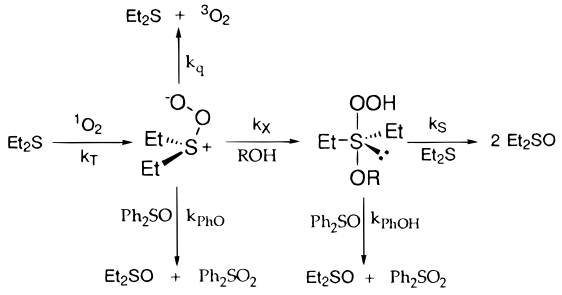


Figure 3. A plot of [Et_2S]$^{-1}$ and [MeOH]$^{-1}$ versus (slope)$^{-1}$ given in Table 4. (□) slope = 3.43; r = 0.999968. (●) slope = 91; r = 0.969386.

Scheme 3



correctly predicts the observed linear relationships. Independent verification that the approximations leading to eq 3a are reasonable was provided by the observations that plots of the inverse of the slopes reported in Table 3 versus 1/[MeOH] and 1[Et_2S] are both linear as predicted by eq 4 (Figure 3).

The slope of the 1/[Et_2S] plot shown in Figure 3 gives k_{PhOH}/k_S = 1.02 which compares favorably to the average value of 2.77 obtained by Foote and co-workers in pure methanol,[1] especially in light of the approximations inherent in this analysis. The slope of the 1/[MeOH] plot shown in Figure 3 gives k_{PhO}/k_X = 182.[15] This number which is clearly an approximation nevertheless suggests that nucleophilic attack at the sulfonium ion-like sulfur in the persulfoxide is an inherently unfavorable process. This observation is undoubtedly responsible for the reluctance of sterically encumbered sulfides to react via

(12) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987.
(13) Mathieu-Pelta, I.; Evans, S. A., Jr. *J. Org. Chem.* **1994**, *59*, 2234−2237.
(14) March, J. *Advanced Organic Chemistry. Reactions Mechanisms and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.

$$\frac{[Et_2SO]}{[Ph_2SO_2]} = 1 + \frac{2k_S k_X[MeOH][Et_2S]}{(k_{PhO}k_S[Et_2S] + k_{PhO}k_{PhOH}[Ph_2SO] + k_{PhOH}k_X[MeOH])[Ph_2SO]} \quad (3)$$

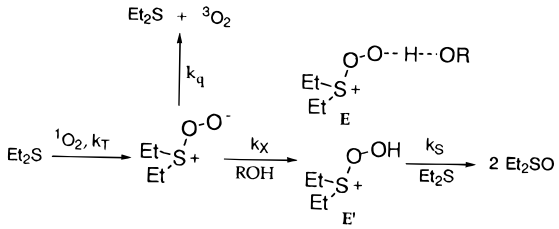
$$\frac{[Et_2SO]}{[Ph_2SO_2]} = 1 + \frac{2k_S k_X[MeOH][Et_2S]}{(k_{PhO}k_S[Et_2S] + k_{PhOH}k_X[MeOH])[Ph_2SO]} \quad (3a)$$

$$\frac{1}{\text{slope}} = \frac{k_{PhO}}{2k_X[MeOH]} + \frac{k_{PhOH}}{2k_S[Et_2S]} \quad (4)$$

the mechanism which has been suggested for the photooxidation of thietane[16] and also provides an explanation for the observation that even in the presence of more than 18 equivalents of methanol (Table 2) 16% of the singlet oxygen is still physically quenched by Et_2S.

The magnitude of k_{PhO}/k_X is inconsistent with any mechanism which involves proton or hydrogen bond activation of the persulfoxide to form a hydroperoxy sulfonium ion, **E** or **E′**, as shown in Scheme 4. The rates

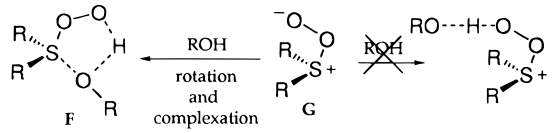
Scheme 4



of protonation and/or hydrogen bond formation are expected to be close to the diffusion limit[17] and as a consequence, and in contrast to the experimental observation, k_{PhO}/k_X is expected to be small for any mechanistic scenario involving these steps.

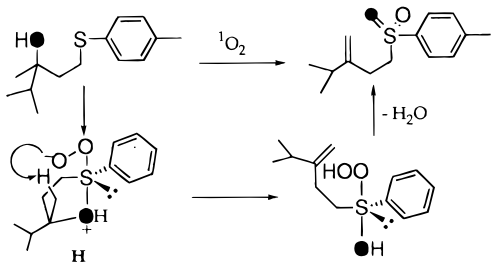
The most reasonable explanation for the experimental data is a "concerted" formation of the sulfurane as depicted in Scheme 2 via the activated complex **F**. This mechanism is consistent with: (1) the observed dependence of $1/k_r$ on 1/[ROH], (2) the large value of k_{PhO}/k_X, and (3) the incipient transfer of a hydrogen to the persulfoxide oxygen in the activated complex which provides an explanation for the experimentally observed dependence on the pK_a of the alcohol. In addition, if proton transfer is advanced in comparison to sulfur−oxygen bond formation little if any steric interaction with the alkyl group on oxygen would be expected (Table 3).

Jensen and Foote[8] pointed out that at the HF/3-21G(*) ab initio level the persulfoxide has C_s symmetry with the oxygen-oxygen bond bisecting the R−S−R angle, **G**. However, a 120° rotational isomer with C_1 symmetry was also located with an energy only 1.2 kcal/mol higher than **G**. This rotational isomer collapsed to a thiadioxirane at the computationally higher MP2/6-31G* level.[9] Consequently, formation of the activated complex **F** in highly protic alcoholic media must involve concomitant rotation and complexation of persulfoxide **G**.



The ultimate formation of a sulfurane is consistent with a large body of earlier work with hydroxy-tethered substrates.[18−20] In particular, photooxidation of the ^{17}O labeled γ-hydroxy sulfide (Scheme 5) resulted in forma-

Scheme 5



tion of unusual olefinic sulfones in which the hydroxy group transferred to sulfur. This observation is consistent with a sulfurane intermediate, **H**, which collapses to a novel hydrated sulfone which serves as the precursor to the olefin.

Conclusion

Our results demonstrate that Et_2S is converted to its oxidized products by different mechanisms in benzene and in benzene/methanol. In both solvents $^1O_2$ reacts with Et_2S to give a persulfoxide whose ultimate destiny is a function of solvent. In aprotic solvents like benzene it is converted to a second intermediate which is most likely a thiadioxirane.[16,21−28] In the protic solvent methanol, however, it is converted to a hydroperoxy-methoxy sulfurane via "concerted" addition of the alcohol which involves rotation of the persulfoxide to the reactive conformation followed by 1,3-dipolar addition across the O-H bond of the alcohol. This concerted addition com-

(15) Foote and co-workers have reported values of k_{PhO}/k_X in benzene where k_X is the rate of interconversion to the thiadioxirane.[1] Their values of 43 and 62 obviously cannot imply that the rate of interconversion to the hydroperoxy sulfurane is slower than the conversion to the thiadioxirane. The difference in the two ratios could be due in large part to k_{PhO} which is undoubtedly different in the two solvents. In particular, hydrogen bonding to the sulfoxide oxygen might make it a better trapping agent in methanol/benzene mixtures than in pure methanol.

(16) Clennan, E. L.; Dobrowolski, P.; Greer, A. *J. Am. Chem. Soc.* **1995**, *117*, 9800−9803.
(17) Denisov, G. S.; Bureiko, S. F.; Golubev, N. S.; Tokhadze, K. G. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; John Wiley & Sons Ltd: New York, 1980; Vol. 2; pp 107−141.
(18) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044−4046.
(19) Clennan, E. L.; Yang, K.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5251−5252.
(20) Clennan, E. L.; Yang, K. *J. Org. Chem.* **1992**, *57*, 4477−4487.
(21) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809−810.
(22) Clennan, E. L.; Wang, D.; Zhang, H.; Clifton, C. H. *Tetrahedron Lett.* **1994**, *35*, 4723−4726.
(23) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952−7954.
(24) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218−4227.
(25) Clennan, E. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT., 1995; Vol. IV, pp 49−80.
(26) Clennan, E. L.; Chen, M.-F. *J. Org. Chem.* **1995**, *60*, 6444−6447.
(27) Clennan, E. L. *Sulfur Rep.* **1996**, *18*, in press.
(28) For an alternative viewpoint on the identity of the second intermediate in benzene see: Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677−2682.

petes with physical deactivation of singlet oxygen and its efficiency can be related to the pK_a of the alcohol.

Experimental Section

General Aspects. Gas chromatographic data were collected on a Hewlett-Packard GC/MS instrument consisting of a 5890 series II GC and a 5971 series mass selective detector, or on a Perkin-Elmer Autosystem. A HP-5 (30 m × 0.25 mm × 0.25 μm (length × inside diameter × film thickness)) capillary column was used on the GC/MS and a 5% diphenyl−95% dimethyl polysiloxane (30 m × 0.32 mm × 1.0 μm (length × inside diameter × film thickness)) fused silica column was used on the Perkin Elmer Autosystem. Benzene (Aldrich, spectral grade) was distilled over P_2O_5 and then stored over activated 4A molecular sieves prior to use. Et_2S (Aldrich, 97%) was purified by refluxing for 1 h with Na metal prior to distillation. 1,2,3,4-Octahydronaphthalene (Δ9(10)-octalin), *meso*-tetraphenyl porphyrin, TPP, and biphenyl were used as received from Aldrich. Diphenyl sulfoxide was recrystallized from hexane−methylene chloride or hexane-ethyl acetate and its purity checked by GC prior to use. Adamantaneadamantylidene was synthesized and purified as reported in the literature.[30] *tert*-Butyl alcohol was stirred overnight with K_2CO_3 and then distilled. All the other alcohols were purified by simple distillation. Oxygen gas was passed over $CaCl_2$ and bubbled into benzene for a minimum of 30 min to obtain a saturated solution.

k_r Determination. The chemical rate constants, k_r, for the Et_2S singlet oxygen reactions in 0.62 M alcohol/benzene mixtures were determined at room temperature by competition with Δ9(10)-octalin from a plot of eq 5 using the procedure previously described.[16] The k_T used for octalin (1.84×10^6 M^{-1} s^{-1}) was previously reported and was set equal to k_r(octalin).[24] The hydroperoxide product formed in the ene reaction of octalin was reduced with a 1−3 molar excess of PPh_3 prior to GC analysis. Control experiments demonstrated that Et_2S did not react with this hydroperoxide under the reaction conditions. A control reaction was also done to verify the inability of PPh_3 to abstract an oxygen atom from Et_2SO. The GC temperature was ramped using the following program: initial oven temperature 80 °C for 10 min, −15 °C/min to 150 °C and held for 6 min, −7 °C/min to 200 °C and held for 9 min, −30 °C/min to 250 °C and held for 15 min. The injector and detector temperatures were held at 250 °C. All concentrations were determined by reference to recently constructed calibration curves.

$$\ln\left(1 - \frac{[Et_2SO + Et_2SO_2]}{[Et_2S]}\right) = \frac{k_r(Et_2S)}{k_r(\text{octalin})} \times \ln\left(1 - \frac{[\text{octalin-OH}]}{[\text{octalin}]}\right) \quad (5)$$

k_T Measurements were determined using the apparatus and procedure previously described.[4,5]

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

Derivation of Equation 2. From eq 2 in the manuscript:

$$k_{r(ROH)} = \frac{2k_{X(ROH)}k_{T(ROH)}[ROH]}{k_q + k_{X(ROH)}[ROH]}$$

solving this algebraically for k_X(ROH) gives:

$$k_{X(ROH)} = \frac{k_q k_{r(ROH)}}{2k_{T(ROH)}[ROH] - k_{r(ROH)}[ROH]}$$

Dividing by a similar expression for k_X(R′OH) gives:

$$\frac{k_{X(ROH)}}{k_{X(R'OH)}} = \frac{k_q k_{r(ROH)}}{k_q k_{r(R'OH)}} \times \frac{(2k_{T(R'OH)} - k_{r(R'OH)})[R'OH]}{(2k_{T(ROH)} - k_{r(ROH)})[ROH]}$$

Since [ROH] = [R′OH] and k_q (the unimolecular microscopic rate constant in Scheme 2) is likely to be unaffected by the identity of the alcohol:

$$\frac{k_{X(ROH)}}{k_{X(R'OH)}} = \frac{k_{r(ROH)}}{k_{r(R'OH)}} \times \frac{(2k_{T(R'OH)} - k_{r(R'OH)})}{(2k_{T(ROH)} - k_{r(ROH)})}$$

Supporting Information Available: A Taft plot for the k_X(rel) values appearing in Table 3 (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(29) A reviewer has expressed the opinion that entropy effects would rule out a concerted addition of ROH to **G** to form **F** and that a mechanism involving two or more ROH molecules, one adding to the sulfur and one providing the proton is more likely. We point out however that the kinetic data is only consistent with the participation of one alcohol. It is not clear that the entropy cost associated with freezing a rotation in **G** is more than entropy cost associated with a termolecular or higher order reaction especially since the entropy cost in the concerted reaction is somewhat compensated by the enthalpically favorable formation of a hydrogen bond.

(30) Fleming, M. P.; McMurray, J. E. In *Organic Synthesis*; Chapman, O. L., Ed.; 1982; Vol. 60, pp 113−117.