solids (0.90 g, 80%): IR (KBr) 1775 cm^{-1}; ^1H NMR (100 MHz, Me_2SO) δ 1.25 (d, 3 H, J = 6 Hz), 2.28 (s, 3 H), 3.36 (br, 2 H), 3.93 (d of q, 1 H, J = 6, 1 Hz), 4.02 (d, 1 H, J = 1 Hz), 4.98 (s, 2 H), 7.11 (d, 2 H, J = 9 Hz), 7.42 (s, 5 H), 7.51 (d, 2 H, J = 8 Hz).

(2*S*-*trans*)-3-[(2,6-Dimethoxybenzoyl)amino]-2-methyl-4-oxo-1-azetidinyl Sulfate, Pyridine Salt (1:1) (37). To a cold (-10 °C) solution of β-lactam salt **35** (0.95 g, 2.5 mM) in methylene chloride (50 mL) were added 2,6-dimethoxybenzoyl chloride (0.60 g, 3 mM) and 4-(dimethylamino)pyridine (0.61 g, 5 mM). The reaction was stirred under nitrogen and allowed to rise to 26 °C over 5 h. The reaction mixture was concentrated to an oil and partitioned between ethyl acetate and aqueous potassium hydrogen sulfate solution. The organic layer was washed with aqueous sodium bicarbonate and brine, then dried over sodium sulfate, and concentrated to a yellow foam (0.843 g, 91.5%): ^1H NMR ($CDCl_3$) δ 1.36 (d, 3 H), 3.66 (m, 1 H), 3.75 (s, 6 H), 4.25 (dd, 1 H, J = 6, 1 Hz), 5.00 (s, 2 H), 7.33 (s, 5 H), 6.50-7.85 (4 H).

To a stirred solution of **36** (0.848 g, 2.28 mM) in absolute ethanol (20 mL) under nitrogen were added 1,4-cyclohexadiene (8 mL) and freshly prepared palladium black (approximately 0.85 g, prepared according to "Organic Syntheses".[28] After 1 h, TLC indicated the absence of starting material, and the reaction mixture was filtered and evaporated to give the *N*-hydroxy β-lactam as a white solid (0.605 g, 94.8%): IR (KBr) 1772, 1657 cm^{-1}; ^1H NMR (CD_3OD) 1.48 (d, 2 H, J = 6 Hz), 3.81 (s, 6 H, overlapping with m, 1 H), 4.33 (d, 1 H, J = 1 Hz), 6.5-7.5 (m, 3 H).

To a solution of the above (0.60 g, 2.14 mM) in dry pyridine (20 mL) under nitrogen were added 4A molecular sieves (approximately 3 mL) and pyridine-sulfur trioxide complex (1.35 g, 8.5 mM). After 3 h, the reaction mixture was filtered, and the filtrate was concentrated and applied to an HP 20-AG resin column (acetone/water). The desired fractions were lyophilized to afford **37** (0.192 g, 20%) as a white powder: IR (KBr) 1776, 1653 cm^{-1}; ^1H NMR (100 MHz, D_2O) δ 1.56 (d, 3 H, J = 6 Hz), 3.83 (s, 6 H), 4.32 (m, 2 H), 6.6-9.0 (m, 8 H, aromatic). Anal. Calcd for $C_{18}H_{21}N_3O_8S \cdot 0.5H_2O$: C, 48.21; H, 4.94; N, 9.37; S, 7.15. Found: C, 48.23; H, 4.94; N, 9.37; S, 7.10.

β-Lactam 42. A suspension of acid **40** (0.879 g, 2.75 mM), *N*-hydroxybenzotriazole (0.42 g, 2.75 mM), and DCC (0.56 g, 2.75 mM) in DMF (15 mL) was stirred at 26 °C for 1 h, at which point a solution of **35** (0.95 g, 2.5 mM) and diisopropylethylamine (0.44 mL, 2.5 mM) in DMF (5 mL) was added. The reaction mixture was stirred at room temperature overnight, then poured into water (100 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with water (3 × 100 mL) and aqueous sodium bicarbonate solution (1 × 100 mL) and then dried over sodium sulfate and concentrated under reduced pressure to a yellow semisolid residue. PLC (EtOAc) afforded the desired product as a yellow foam (0.599, 47%), which recrystallized from $CHCl_3$/isopropyl ether: mp 100-105 °C; IR (KBr) 1768, 1712, 1672 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.12 (d, 3 H, J = 6 Hz), 1.16 (t, 3 H, J = 4 Hz), 3.54 (m, 6 H), 4.02 (m, 2 H), 4.31 (dd, 1 H, J = 1, 6 Hz), 4.91 (s, 2 H), 5.44 (d, 1 H, J = 6 Hz), 7.32 (s), 7.37 (s).

β-Lactam 41. In a similar manner **35** (0.95 g, 2.5 mM) was reacted with acid **30** (0.55 g, 2.75 mM) to give, after chromatography, **41** as a yellow foam (0.643 g, 46%), which crystallized from $CHCl_3$/isopropyl ether: mp 90-105 °C slow dec; IR (KBr) 1765, 1667 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.12 (d, 3 H, J = 6 Hz), 3.68 (d of q, 1 H, J = 6, 1 Hz), 3.92 (s, 3 H), 4.56 (dd, 1 H, J = 1, 6 Hz), 4.98 (s, 2 H), 5.55 (br, 2 H), 6.76 (s, 1 H), 6.78 (s, imp ?), 7.37 (s, 5 H), 8.12 (d, 1 H).

[2*S*-[2α,3β(*R)]]-3-[(((((4-Ethyl-2,3-dioxo-1-piperazinyl)carbonyl)-amino)phenylacetyl)amino]-2-methyl-4-oxo-1-azetidinyl Sulfate, Pyridine Salt (1:1) (43).** An ethanolic solution (25 mL) of **42** (0.270 g, 0.53 mM) containing 10% Pd/C (130 mg) was hydrogenated at atmospheric pressure for 2 h. The reaction mixture was filtered and concentrated to a white sticky solid (0.220 g, 99%), which was used directly. To a solution of the above (0.220 g, 0.53 mM) in pyridine (7 mL) were added 4A molecular sieves (approximately 1 mL) and pyridine-sulfur trioxide complex (0.33 g, 2.1 mM). After being stirred under nitrogen at 26 °C for 4.5 h, the reaction mixture was filtered and concentrated to an oil. Chromatography on HP 20-AG resin H_2O/acetone) followed by lyophilization of the appropriate fractions afforded the desired product as a white powder (0.080 g, 25%): IR (KBr) 1780, 1723, 1677 cm^{-1}; ^1H NMR (100 MHz, D_2O) δ 1.19 (t, 3 H, J = 7 Hz), 1.44 (d, 3 H, J = 6 Hz), 3.52 (q, 2 H, J = 7 Hz), 3.68 (m, 3 H), 4.01 (m, 4 H), 4.54 (d, 1 H, J = 2 Hz), 5.46 (s, 1 H), 7.48 (s, 5 H), 8.10-9.0 (m, 5 H); TLC R_f 0.63 $CHCl_3/CD_3OD/HCO_2H$ (70:30:2), 0.42 *n*-BuOH/HOAc/H_2O (60:20:20), 96-99% pure by spectrodensitometry. Anal. Calcd for $C_{24}H_{28}N_6O_9S \cdot 2.2H_2O$: C, 46.78; H, 5.19; N, 13.63. Found: C, 46.36; H, 4.74; N, 13.42.

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Registry No. 1, 71405-00-0; **2**, 82933-24-2; **3**, 75624-37-2; **4**, 82933-25-3; **5**, 82933-27-5; **7**, 82933-28-6; **8**, 82933-31-1; **8** benzyl ether, 82933-33-3; **9**, 82933-35-5; **10**, 82933-36-6; **13**, 71404-99-4; **14**, 82933-30-0; **15**, 82933-37-7; **16**, 76530-06-8; **17**, 82933-42-4; **18**, 26048-92-0; **19**, 82933-43-5; **21**, 82933-44-6; **22**, 28832-02-2; **23**, 82933-40-2; **24**, 82933-38-8; **25**, 82933-39-9; **29**, 82951-09-5; **30**, 82933-61-7; **32**, 7685-70-3; **33**, 82933-45-7; **33** mesylate, 82933-47-9; **34**, 82933-46-8; **35**, 82933-50-4; **36**, 82933-53-7; **36**-ol, 82933-54-8; **37**, 82933-52-6; **39**, 82933-48-0; **40**, 82933-56-0; **41**, 82933-57-1; **42**, 82933-55-9; **43**, 82933-59-3; **42**-ol, 82933-60-6; i, 75624-38-3; ii, 82951-08-4; L-*N*-(phenylacetyl)serine, 2752-53-6; *N*-(phenylacetyl)-L-threonine, 2798-50-7; *N*-(phenylacetyl)-L-threonine *O*-benzylhydroxyamide, 82933-32-2; phenylacetyl chloride, 103-80-0; L-threonine, 72-19-5; *O*-benzylhydroxylamine hydrochloride, 2687-43-6; *o*-nitrobenzenesulfenyl chloride, 7669-54-7; 2,6-dimethoxybenzoyl chloride, 1989-53-3; Cbz-L-serine, 1145-80-8; Pen G K salt, 113-98-4.

Chemistry of Singlet Oxygen. 38. Temperature Effect on the Photooxidation of Sulfides[1]

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Abstract: The reactivity of diethyl sulfide with singlet oxygen has been determined at room temperature (23-24 °C) and at -78 °C in various solvents. Although the consumption of sulfide is much faster at -78 °C, the rate of removal of singlet oxygen by sulfide is relatively independent of solvent and temperature. A comparison of the rate of product formation with the rate of singlet oxygen removal shows that over 97% quenching is observed in aprotic and about 10% in protic solvents at room temperature. At -78 °C, the quenching process is suppressed in both protic and aprotic solvents. Surprisingly, 2,5-diphenylfuran showed a similar but much smaller effect of solvent and temperature.

Sulfides have been shown to have very large and surprising effects of solvent and temperature on their reactions with singlet oxygen. Foote and Peters[2,3] found that in protic solvents the reaction rates do not vary much with temperature but that in

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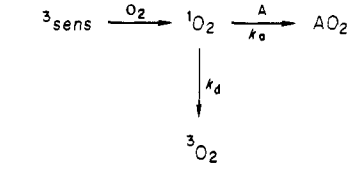
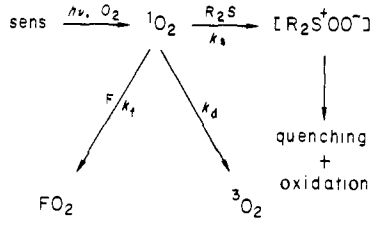
Scheme I



Scheme II



aprotic solvents product formation is much faster at low temperature than at room temperature.

It is also known that sulfides give products much faster with singlet oxygen in protic solvents than in aprotic solvents at room temperature.[2,3] The rate of total removal of $^1O_2$ by sulfide, however, is almost the same in both classes of solvent.[3,4]

Recently, indenes have been shown to be photooxidized faster at low temperature than at room temperature[5-7] in a behavior very similar to that of sulfides (Scheme I). However, the product distribution is very complicated and depends on the temperature, solvent, and sensitizer used.[5-8]

In an attempt to determine the activation energy of reaction of a series of olefins and dienes with singlet oxygen, Koch[9] investigated the effect of temperature on reaction rates and found that in the range of +50 to −150 °C, the quantum yield of oxygen consumption by olefins and dienes follows a simple rate law. By measuring the value of β (the ratio of rate constants for singlet oxygen decay, k_d, to reaction, k_a), he concluded that k_d is practically independent of temperature and that k_a for reactive compounds has only a small activation energy.

Kearns[10,11] applied the laser flash photolysis technique originally developed by Wilkinson[12] to measure the lifetime of singlet oxygen directly. From the reaction of DPBF (diphenylisobenzofuran) with singlet oxygen in chloroform, Kearns[13] observed a 2-fold increase in k_a from −50 to +25 °C, which was attributed to the change in viscosity of chloroform with temperature. The singlet oxygen lifetime ($1/k_d$) decreased 50% over the same temperature range.

In a similar attempt to measure the activation energy for singlet oxygen reactions by using pulse radiolysis techniques, Rogers[14] found a zero activation energy for the reaction of furans and indoles with singlet oxygen. A 20% singlet-oxygen-lifetime decrease in the temperature range of −50 to +25 °C was observed in toluene. From the studies reported above, the apparent large increase in reactivity of sulfides on cooling cannot be due to an effect on k_d, and k_a would (if anything) be expected to increase slightly at higher temperature. Thus, the dramatic increase in reactivity of sulfides in aprotic solvents on cooling and the low reactivity at room temperature in aprotic solvents compared to that of protic solvents were suggested to be caused by quenching of singlet oxygen in aprotic solvents at room temperature. Foote and Peters[2,3] suggested that this quenching process is suppressed at low temperature or in protic solvents to account for the 30–100-fold increase in rate of product formation, although no kinetic studies to demonstrate this were carried out. A detailed kinetic study of sulfide photooxidation at low temperature was thus necessary to test this suggestion.

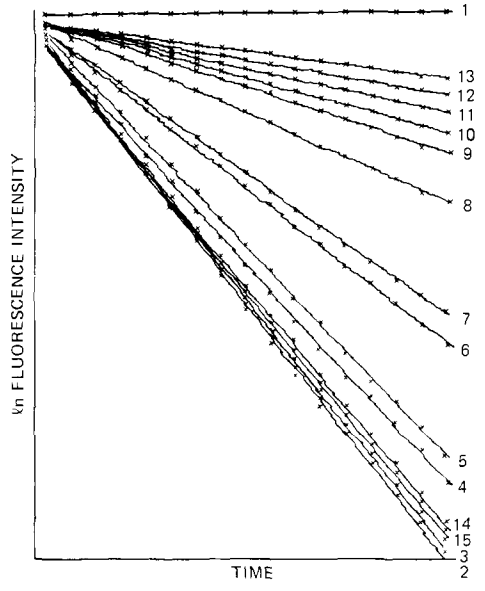


Figure 1. Typical display of logarithm of raw fluorescence intensities as a function of time at different diethyl sulfide concentrations.

Results

Temperature Effect on the β Values of Diethyl Sulfide Photooxidation. Scheme II (based on Young's method[15] and the proposed mechanism for sulfide photooxidation[2-4]) was applied to determine the reactivity of sulfides toward singlet oxygen at various temperatures. In this scheme, K_t is the rate of formation of singlet oxygen, k_s is the rate constant for reaction of singlet oxygen with the sulfide, and k_f is the rate constant for reaction of singlet oxygen with the acceptor, whose disappearance can be monitored by its fluorescence. In this scheme, the solvent dependence would occur after the formation of initial persulfoxide intermediate,[16] and β would not be affected by solvent change (except as it affects k_d), as confirmed by Foote and Peters.[2,3]

Under steady-state conditions, the disappearance rate of the fluorescer F is

$$\frac{-d[F]}{dt} = \frac{K_t k_f [F]}{k_f[F] + k_d + k_s[R_2S]} \quad (1)$$

When a sufficiently low concentration of F is used, $k_f[F]$ becomes negligible compared to $(k_d + k_s[R_2S])$, and eq 1 simplifies to eq 2.

$$\frac{-d[F]}{dt} = \frac{K_t k_f [F]}{k_d + k_s[R_2S]} \quad (2)$$

Integrating eq 2:

$$-\ln F/F_0 = \frac{K_t k_f}{k_d + k_s[R_2S]} t \quad (3)$$

(1) Paper No. 37: Manring, L. E.; Foote, C. S. *J. Phys. Chem.* **1982**, *86*, 1257. Supported by NSF Grants No. CHE 77-21560 and 80-20190.
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Table I. Summary of Results from β-Value Determinations of Diethyl Sulfide

solvent	sens	T, °C	β value, M × 10³	S_B^a × 10¹	$10^{-7}k_s$, M^{-1} s^{-1}
toluene	ZnTPP	RT[b]	2.92 ± 0.21	0.88	1.37[c]
acetone	RB	RT	0.89 ± 0.10	0.79	2.69[d]
acetone	RB	−78	0.97 ± 0.04	2.18	e
ether	ZnTPP	RT	6.02 ± 0.04	1.18	e
ether	ZnTPP	−78	4.07 ± 0.66	5.37	e
methanol	RB	RT	6.65 ± 0.75	1.15	1.66[f]
methanol	RB	−78	10.60 ± 0.20	1.61	e

[a] S_B is the average slope of blank runs ($-\ln F$ vs. t). For the same solvent, the same lamp power was applied; however, S_B values are only comparable within a given solvent because of changes in lamp power, light absorption, and sensitizer in different solvents. [b] RT = 23–24 °C. [c] $k_d = 4.0 \times 10^4$ s^{-1} (ref 18). [d] $k_d = 2.4 \times 10^4$ s^{-1} (ref 19). [e] No literature value of k_d is reported. [f] $k_d = 1.1 \times 10^5$ s^{-1} (ref 19).

where F and F_0 are the fluorescence intensity of F at time t and time 0. The slope of the first-order plot of $-\ln F/F_0$ vs. t will be

$$S_1 = \frac{K_t k_f}{k_d + k_s[R_2S]} \quad (4)$$

In the absence of sulfide substrate, the slope (S_B) becomes

$$S_B = K_t k_f / k_d \quad (5)$$

Dividing eq 5 by eq 4 gives

$$S_B/S_1 = 1 + (1/\beta)[R_2S] \qquad (\beta = k_d/k_s) \quad (6)$$

A plot of S_B/S_1 vs. $[R_2S]$ gives the β value. 2,5-Diphenylfuran was used as the fluorescer. A typical computer plot of the raw data of the logarithm of the fluorescence intensity of F at different diethyl sulfide concentrations is shown in Figure 1. As will be seen, excellent first-order kinetics are observed. Run 1 is a "dark run" with the photolyzing light (absorbed by the sensitizer) off and measures the self-sensitized decay of F by the fluorescence excitation light alone. Runs 2, 3, 14, and 15 are blank runs with no substrate present and are averaged to calculate S_B. The rest of the runs have different sulfide concentrations. The slopes of the lines are S_1 and are determined by computer analysis; computer plots of S_B/S_1 vs. $[Et_2S]$ are fit with a straight line by the method of least squares. An example of such a plot is given in Figure 2.

The reactivity of diethyl sulfide toward singlet oxygen at room temperature (23–24 °C) or −78 °C in various solvents was determined by using the method described above. Because toluene solutions became cloudy at −78 °C (probably due to water precipitation), only room-temperature results were obtained. In ether, acetone, and methanol, no cloudiness was observed, and both room-temperature and low-temperature (−78 °C) results are given. Table I summarizes the results. The k_s values are also given in Table I when k_d is available from the literature. In order to compare S_B values of 2,5-diphenylfuran at room temperature and −78 °C for each solvent, we measured the S_B values in Table I at the same lamp power. (The actual S_B values used for the β-value determination were measured under different conditions.)

Temperature Effect on the Rate of Product Formation of Diethyl Sulfide Photooxidation. In order to compare the rate of product formation in sulfide photooxidation as a function of temperature, we photolyzed diethyl sulfide in three different solvents (acetone, ether, and methanol) at room temperature (23–24 °C) or −78 °C to less than 20% conversion and measured the amount of product by GLC. Table II summarizes the GLC results.

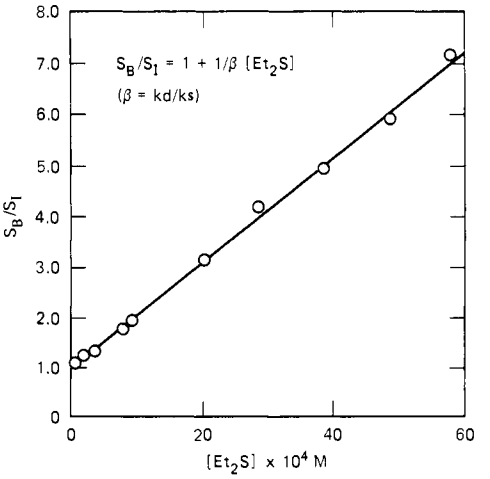
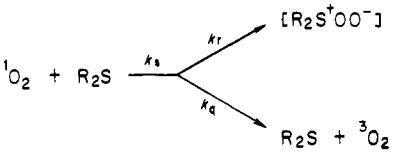


Figure 2. Plot of S_B/S_1 vs. $[Et_2S]$ for diethyl sulfide in acetone at −78 °C.

Scheme III



Discussion

For photooxidation of diethyl sulfide in aprotic solvents, a 30–50-fold increase in the rate of product formation was observed when the reaction temperature was lowered from room temperature to −78 °C (Table II). Foote and Peters[2,3] observed an approximate 5-fold increase for diethyl sulfide (0.02 M) in ether and over a 100-fold increase for 1,4-dithiane in the same temperature range. Thus, qualitatively, sulfides do react much faster at low temperature than at room temperature in aprotic solvents. In methanol, only a 10% increase was observed in the same temperature range, in good agreement with the previous result.[3]

The rate of reaction of diethyl sulfide with singlet oxygen, k_s, in methanol at room temperature is 1.66×10^7 M^{-1} s^{-1} (Table I), in excellent agreement with that measured by Kacher[4] (1.71×10^7 M^{-1} s^{-1}). Although the value of k_s in ether cannot be calculated by this study because the rate constant of singlet oxygen decay (k_d) is not available, it is clear from values in toluene, acetone, and methanol that k_s is relatively insensitive to the solvent used.

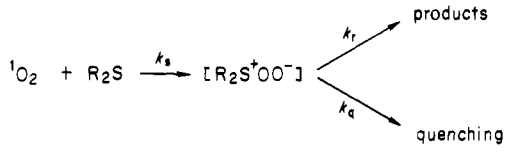
No significant difference in the β values for the reaction of diethyl sulfide with singlet oxygen in a given solvent was found at room temperature and −78 °C (Table I). Although the singlet-oxygen lifetime ($1/k_d$) has been reported to increase slightly

Table II. GLC Determination of Products from the Reaction of Diethyl Sulfide with Singlet Oxygen at RT[a] and −78 °C

$[Et_2S]$, M × 10³	T, °C	irradiation time, min	product $[Et_2SO]$, M	product $[Et_2SO_2]$, M	ratio of rate at RT to −78 °C	% quenching at RT[a,f]
3.77[b]	RT[a]	30	2.15×10^{-4}	g		
3.77[b]	−78	4	1.17×10^{-3}	1.10×10^{-4}	1/45	97.8
4.50[c]	RT[a]	30	1.71×10^{-4}	2.11×10^{-5}		
4.50[c]	−78	3	5.20×10^{-4}	7.20×10^{-5}	1/34	97.0
4.51[d]	RT[a]	2	1.20×10^{-3}	g		
4.51[d]	−78	2	1.25×10^{-3}	9.06×10^{-5}	9/10	10.0

[a] RT = 23–24 °C. [b] Acetone, [RB] = 1.70×10^{-5} M. [c] Ether, [ZnTPP] = 1.00×10^{-4} M. [d] CH_3OH, [RB] = 1.70×10^{-5} M. [e] Rate of product formation corrected for irradiation time. [f] Assume no quenching at −78 °C (see text). [g] Concentration too low to measure.

Scheme IV

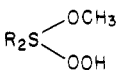


at low temperature,[18,19] the largest change reported was a factor of 2 over a 100 °C temperature range. Thus, quenching must be suppressed at low temperature in aprotic solvents in order to explain the large increase in product formation on going from room temperature to −78 °C. If quenching (k_q) and reaction (k_r) of sulfide toward singlet oxygen are parallel reactions proceeding directly from sulfide (Scheme III), then the measured k_s equals $k_r + k_q$ and should vary significantly with temperature (unless k_r and k_q vary inversely, which is very unlikely), contrary to the experimental results (Table I). Thus, quenching must occur after the formation of the primary intermediate. If we assume there is no quenching at −78 °C, then ≥97% quenching is calculated in aprotic solvents at room temperature (Table II), in good agreement with Peters' results.[3] The fact that ≥97% quenching is observed for all the aprotic solvents used suggests that the proposed mechanism for sulfide photooxidation in benzene (Scheme IV) is probably similar in ether and acetone.

The decreased quenching at low temperatures is reasonably explained by stabilization of intermediate **1**, resulting in an increase in the ratio of k_r to k_d. The k_q process appears to be simply loss of O_2 from intermediate **1**.

The ratio of the rate of sulfide photooxidation in methanol at room temperature to that at −78 °C equals 0.9, which means that if at −78 °C there is no quenching (reaction only), then 10% quenching occurs at room temperature, in good agreement with the results from kinetic experiments.[16,17]

The effect of protic solvent in suppressing quenching appears to result from a stabilization of the reactive intermediate, either by hydrogen bonding or by actual addition to give a sulfurane (**2**).



2

Detailed kinetic studies have just been completed and are consistent with either hypothesis.[20]

The slope of blank runs ($S_B = K_1k_f/k_d$) for 2,5-diphenylfuran increases by a factor of 2.7 in acetone and 4.6 in ether when the temperature decreases from room temperature to −78 °C (Table I). Since the intersystem crossing efficiencies of rose bengal[21] and ZnTPP[22,23] are very large at room temperature (≳0.8) and singlet-oxygen lifetime ($1/k_d$) and the rate of reaction of furan and singlet oxygen do not change significantly with temperature,[13,14] there may also be a small amount of quenching at room temperature for the 2,5-diphenylfuran reaction with singlet oxygen. Interestingly, S_B of 2,5-diphenylfuran only increases 1.5 times in methanol over the same temperature range. The small increase of S_B at low temperature can be explained by the increase of singlet-oxygen lifetime at low temperature, which means that quenching is not occurring in methanol. Such a solvent effect on quenching is similar to that for sulfide photooxidation, but smaller.

Foote[24] and Kearns[11] showed that diphenylisobenzofuran does not quench singlet oxygen appreciably without reaction in either protic or aprotic solvents. Foote[24] also argues that there is no quenching in methanol for 2-methyl-2-pentene, *cis*-4-methyl-2-pentene, and diphenylanthracene on the basis of the identical values obtained for $k_a + k_q$ and k_a from different methods. From this study, it is suggested that some quenching may occur in the photooxidation of furans in aprotic solvents. However, because S_B values include effects of sensitizer intersystem crossing and light absorption (which are cancelled in the β-value determination of the sulfide), detailed studies of the temperature effect on the rates of reaction and quenching of singlet oxygen as well as on the lifetime of singlet oxygen are needed to clarify quantitatively the nature of the temperature effect on furan reactions.

In conclusion, this study shows that in sulfide photooxidation, the rate of removal of singlet oxygen by sulfide is relatively independent of solvent and temperature. At room temperature, over 97% quenching is observed in aprotic solvents but only 10% quenching in protic solvents. At low temperature (−78 °C), the quenching is suppressed in both protic and aprotic solvents.

Experimental Section

General Methods. Diethyl sulfide was distilled over Na. Ether and Spectrograde methanol were used as received. Spectrograde acetone was treated with molecular sieves before use. Benzene and toluene were distilled over phosphorus pentoxide. Rose bengal and zinc tetraphenylporphine (ZnTPP) were recrystallized before use. For photooxidation of diethyl sulfide, the reaction flask was kept in a half-silvered Dewar with a water-cooled 650-W Sylvania Tungsten Halogen lamp as the light source. All product analysis was performed with GLC by using either 3% or 10% Carbowax 20M on 100/200 Chromosorb 6 ft × $^1/_8$ in. chromatographic columns. Hexamethylbenzene or diphenylmethane was added as internal standard.

Fluorescence-Monitored Kinetic Measurements. The basic setup for fluorescence-monitored reaction kinetic measurements has been described elsewhere.[24,25]

2,5-Diphenylfuran was used as the fluorescent compound. The excitation wavelength was set at 335 nm, and the fluorescence was monitored at 371 nm. Rose bengal (8.5×10^{-6} M) and ZnTPP (2×10^{-5} M) solutions were photolyzed through Corning CS-3-68 and CS-3-72 filters, respectively. All runs used the same concentrations of 2,5-diphenylfuran (3.0×10^{-6} M) and sensitizer. All samples containing different concentrations of the substrate were saturated with oxygen before being pipeted into a modified 1-cm quartz cell transparent on all sides. A small overhead stirrer with a glass rod was used to keep the solution homogeneous during the photolysis period. Positive oxygen pressure was provided on top of the modified cell.

When a low-temperature experiment was performed, an S-shaped Dewar tube designed originally by P. Ogilby was used.[26] One end was immersed in a liquid nitrogen Dewar flask equipped with a resistor to boil off the liquid nitrogen; the other had an unsilvered area to allow the light to pass to the sample cell. The cooled gas passed through the Dewar tube and over the sample cell. A UCLA 3819A temperature controller equipped with a thermistor sensor in the gas stream controlled a heater to adjust the temperature of the flowing gas to maintain a constant temperature in the cell. A Newport 26DC2 temperature readout was used to record the temperature. All samples were allowed to reach constant temperature before the photolysis.

Registry No. Et_2S, 352-93-2; Et_2SO, 70-29-1; Et_2SO_2, 597-35-3; ZnTPP, 14074-80-7; oxygen, 7782-44-7; 2,5-diphenylfuran, 955-83-9; rose bengal, 11121-48-5.

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