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Persulfoxide and Thiadioxirane Intermediates in the Reaction of Sulfides and Singlet Oxygen

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Abstract: Structure and reactivity of intermediates in the reaction of sulfides and singlet oxygen have been studied in aprotic solvents. It is shown that sulfoxides and sulfones are the major products at the initial stage of reaction. While the sulfoxide formation is more sensitive to the electronic effect of substituents, the steric retardation is more significant for sulfone formation. The effect of additives also revealed the sharp contrast between the two reactions; sulfoxide formation is accelerated significantly by protic or coordinating solvents, but sulfone formation is never affected by additives. ^{18}O-tracer experiments indicated that the two oxygen atoms in sulfones come from one oxygen molecule. The apparent activation energy for sulfone formation is positive in contrast to the sulfoxide case. These facts suggest that thiadioxirane intermediates are surely formed via a nonpolar reaction in competition with persulfoxide formation. It is also shown that persulfoxides are stabilized by coordinating solvents as well as by protic ones. The stability of thiadioxiranes is discussed on the basis of theoretical calculations.

The photooxidation of organic sulfur compounds has been extensively studied from mechanistic[1] and biological interests.[2] Thoroughly reported are singlet oxygen oxidations of dialkyl,[3,4] diaryl,[5] vinyl,[6] and allyl sulfides,[7] thiiranes,[8] and disulfides.[9] In relation to the chemistry of carbonyl[10] and nitroso oxides,[11] we became interested in the structure and reactivity of persulfoxide intermediates in the photooxidation of sulfides.[12]

In the reaction of singlet oxygen with sulfides, the peroxidic intermediates (PI) react with the second sulfide molecule as shown in eq 1. Singlet oxygen is shown to react electrophilically with

$$R_2S + {}^1O_2 \rightarrow PI \xrightarrow{R_2S} 2R_2SO \qquad (1)$$

sulfides as judged from the Hammett ρ-value of -1.6 for the $^1O_2$ quenching by substituted aryl sulfides.[5] Dipolar persulfoxide (**1**), diradical **1′**, and thiadioxirane intermediates (**2**) could be written as candidates of PI. Foote et al.[4] have elegantly suggested the

$R_2S^+{-}O{-}O^-$

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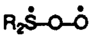
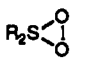


$R_2\dot{S}{-}O{-}\dot{O}$

1′



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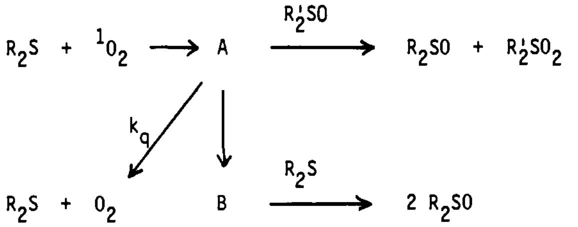
dipolar structure **1** on the basis of the dramatic effect by protic solvents. Thence, the dipolar structure **1** has been often written in the photooxidation of sulfides.[13] Trapping experiments suggested that persulfoxide intermediates oxidize sulfoxides, in contrast to the oxidation of sulfides,[14] nucleophilically (i.e., $\rho >$ 0 for substituted sulfoxides), supporting the dipolar structure.[12] Recently, the structure of **1** has been ascertained by IR spectroscopy in low-temperature matrices.[15]

Scheme I



In the $^1O_2$ oxidation of sulfides, the diradical structure **1′** is not important because of no observation of hydrogen abstraction from solvents or additives. The formation of sulfones as a minor (e.g., <5%) reaction in the photooxidation of sulfides could be evidence for cyclic thiadioxirane (**2**); but the sulfone formation might be explained by the further reaction of sulfoxides with **1**. Thus, the intervention of cyclic **2** has not been clarified.

Detailed trapping kinetics by Foote et al.[16] revealed contrasting behavior of PI's between protic and aprotic solvents. In methanol, only one intermediate was involved that oxidizes sulfides and sulfoxides competitively. In contrast, aspects in aprotic solvents were as follows: (1) Physical quenching of $^1O_2$ is the predominant reaction, and the chemical oxidation is as low as 5%. (2) At low temperature, the physical quenching is reduced, and the yields of oxygenated products increase.[17] (3) Sulfides and sulfoxides are oxidized by two different intermediates. These results are summarized as Scheme I where A and B are nucleophilic and electrophilic oxidants, respectively. Persulfoxides (**1**) and thiadioxiranes (**2**) might be tentatively regarded as the two intermediates, but no confirmation could be obtained. In contrast, it has recently been reported that ab initio molecular orbital (MO) calculations predicted no stable cyclic structure as **2**.[18]

We were interested in the possible intermediacy of **2** and noticed the formation of sulfones as a key product from **2**. The present paper[19] shows that **1** and **2** are equally important intermediates on the basis of effects of additives and substituents, ^{18}O-tracer experiments, and theoretical calculations.

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Table I. Relative Rate for the $^1O_2$ Oxidation of Sulfides **3** to Sulfoxides and Sulfones in Benzene[a]

sulfide[b] RSR'	rel rates of consumptn[c]	product ratios[d] RSOR':RSO$_2$R'	rel rates for formation[e] RSOR'	rel rates for formation[e] RSO$_2$R'
OctSMe (**3a**)	73	71:29	76	66
(n-Bu)$_2$S (**3b**)	59	71:29	61	53
(t-Bu)$_2$S (**3c**)	5.7	90:10	7.5	1.8
PhS-t-Bu (**3d**)	<0.01		<0.01	<0.01
PhS-i-Pr (**3e**)	0.17	93:7	0.23	0.05
PhSMe (**3f**)	1.00	68:32	(1.00)	(1.00)
p-ClPhSMe (**3g**)	0.78	74:26	0.85	0.63
m-ClPhSMe (**3h**)	0.82	62:38	0.75	0.97
p-MeOPhSMe (**3i**)	14	91:9	19	3.9

[a] The photooxidation of 0.05 M RSR' and 0.1 mM TPP in benzene, irradiated at ≥400 nm under oxygen. [b] Key: Oct, n-C_8H_{17}; Ph, C_6H_5 for **3d–f** and C_6H_4 for **3g–i**. [c] The relative rates of sulfide consumption were determined from a time for 1% conversion using a merry-go-round apparatus. [d] Product ratios at the initial stage of oxidation were determined by extrapolation to time = 0 in the plots of the ratios vs time. [e] Relative rates for the formation of sulfoxides and sulfones were calculated from the consumption rates and product ratios in comparison to that of **3f**.

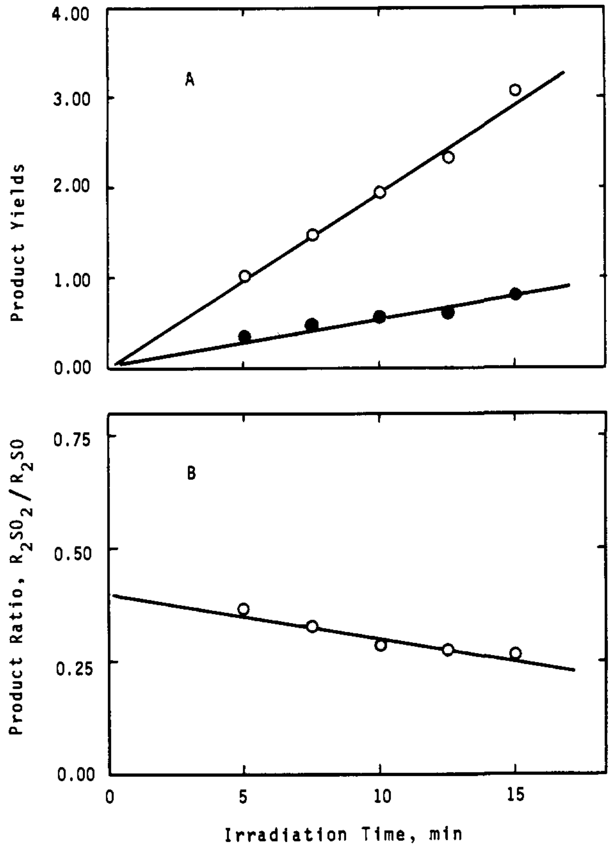

Figure 1. Time curve for the $^1O_2$ oxidation of dibutyl sulfide (**3b**) in benzene. For conditions, see footnote *a* in Table I. Key: A, product yields of Bu$_2$SO (○) and Bu$_2$SO$_2$ (●) vs time; B, product ratios of Bu$_2$SO$_2$/Bu$_2$SO vs time.

Results

Substituent Effect for the Formation of Sulfones and Sulfoxides. In the $^1O_2$ reaction of sulfides, the sulfone formation has not been noticed because of their low yields (e.g., below 5%) at the final stage of reaction. However, sulfones and sulfoxides were two major products at the initial stage of photooxidation as exemplified in Figure 1 for the photooxidation of dibutyl sulfide in benzene irradiated in the presence of tetraphenylporphin (TPP) at >400 nm under oxygen. Although the product ratio, R_2SO_2/R_2SO, decreases gradually with the progress of reaction, the intercept at time zero in Figure 1B corresponds to approximately a 1:2 ratio. If the sulfone was formed according to a sequence $R_2S \rightarrow R_2SO \rightarrow R_2SO_2$, the ratio of R_2SO_2/R_2SO would be expected to increase with the progress of reaction. This was not the case.

Relative oxygenation rates of sulfides **3** in benzene have been determined from times for 1% conversion by use of a merry-go-round apparatus. The resulting rate and product ratios are listed in Table I. The relative rate order of **3a** > **3b** ≫ **3c** and PhSMe > PhS-i-Pr ≫ Ph-t-Bu indicates clearly a significant steric effect for the oxygenation. Selectivities for sulfone formation changed from 38 to 7% depending on substituents as listed in the third column in Table I. The data in the last two columns are relative rates for the formation of sulfoxides and sulfones. It is interesting to note that the steric effect of substituents is more significant for the sulfone formation; cf. ratios for **3c** and **3e**.

Table II. Effect of Additives on the $^1O_2$ Oxidation of Sulfide **3a** in Benzene[a]

additive[b]	product yields (%)[c] RSOR'	product yields (%)[c] RSO$_2$R'
none	1.8	0.63
MeOH	12.3	0.56
t-BuOH	6.2	0.42
DMF	5.3	0.46
DMSO	5.6	0.57
HMPA	4.8	0.55
MeCN	1.9	0.58
MeCN (50 vol %)[d]	21.9	0.53
MeCN (50 vol %)[d,e]	34.6	0.60

[a] Benzene solutions of 0.05 M **3a** and 0.1 mM TPP were irradiated for 10 min at ≥400 nm under oxygen. [b] Additives of 0.1 M concentration were added. Key: DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; HMPA, hexamethylphosphoramide. [c] Products were determined by GLC just after 10 min of irradiation. Determinations were averaged two or three times, probable errors being ±5%. [d] PhH:MeCN = 1:1 in volume. [e] 0.1 M $Bu_4N{\cdot}ClO_4$ was added.

The relative rates for thioanisoles **3f–i** are correlated with Hammett's σ-constants. The resulting ρ-values for the sulfoxide formation are -1.36 (vs σ; $r = 0.77$) and -1.29 (vs σ^+; $r = 0.96$), and those for the sulfone formation are -1.14 (vs σ; $r = 0.73$) and -0.60 (vs σ^+; $r = 0.89$),[20] r being the correlation coefficients. The correlations are much better with σ^+ constants and the electronic effect is more significant for the sulfoxide formation. It is interesting to remember that the reported ρ-value for $^1O_2$ quenching by thioanisoles is -1.6 correlated with σ.[5]

The combined yields of R_2SO and R_2SO_2 from the $^1O_2$ reaction of R_2S were ≥80% in benzene and ≥90% in acetonitrile. The accompanying minor reaction in aprotic solvents is the cleavage of C–S bonds.[13a] For example, octanal was obtained in 8 and 2% yields from the $^1O_2$ reaction of **3a** in benzene and acetonitrile, respectively. This C–S cleavage reaction is not discussed further in the present paper.

Effect of Additives. It is known that physical quenching (k_q) of $^1O_2$ by sulfides is the major pathway in aprotic solvents, while the chemical reaction (k_r) to afford sulfoxides is almost quantitative in protic solvents.[21] Under the present conditions (i.e., 0.05 M **3a** and 0.1 mM TPP under O_2), the quantum yields for product formation were 0.012 and 0.98 in benzene and MeOH–PhH

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(20) For σ and σ^+ values, see: Exner, O. In *Advances in Linear Free Energy Relationship*: Chapman, N. B., Shorter, J., Ed.; Plenum Press: New York, 1972; p 1.

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Table III. ^{18}O-Tracer Study on the Sulfone Formation[a]

sulfide RSOR'	irradiation time	product yield (%)		mass data of RSO_2R'[b]			retention[c] (%)
		RSOR'	RSO_2R'	M	M + 2	M + 4	
3f	10 h	5.2	1.1	100	7.0 ± 0.3	6.4 ± 0.5	93
				(100	5.6 ± 0.2	0.0)[d]	
					(17.9 ± 4.6	82.1 ± 6.4)[e]	
3f	15 h	13.9	1.7	100[f]	79.8 ± 2.5	51.5 ± 2.2	90
				(100[f]	65.2 ± 0.6	0.0)[d]	
					(22.1 ± 3.9	77.9 ± 3.3)[e]	
3a	10 min	5.2	0.7	100[f]	66.1 ± 4.2	53.1 ± 1.5	91
				(100[f]	52.4 ± 2.0	0.0)[d]	
					(20.5 ± 7.0	79.5 ± 2.2)[e]	
calcd for retention					6.7	93.3	100
calcd for scrambling					96.0	4.0	0

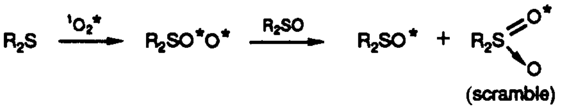
[a] Irradiation of 0.05 M sulfide and 0.1 mM TPP in benzene at ≥400 nm under oxygen gas; $^{32}O_2$:$^{34}O_2$:$^{36}O_2$ = 1:0.006:0.084. [b] Mass spectral data of sulfones by GC-MS; M means parent peak. [c] Retention means that the two oxygen atoms in sulfone are originated from one O_2 molecule. Scramble means that two oxygen atoms come from two different O_2 molecules. See Experimental Section for details. [d] Mass spectral data of authentic sample prepared from RSR' and *m*-chloroperbenzoic acid. [e] The M + 2 values were corrected by abstracting those of natural abundance of RSO_2R'. Hence, the M + 2 and M + 4 values mean the contents of ^{18}O in sulfone. [f] M + 1 values in place of M ones.

(2:1).[22] These data suggest again that the chemical conversion is almost quantitative in protic solvents but is a minor reaction in aprotic solvents.

In order to clarify the role of solvents, the effect of additives was examined in the $^1O_2$ reaction with **3a** in benzene. As shown in Table II, the sulfoxide yields at 10 min of irradiation changed significantly by the presence of 0.1 M additives. As expected, 0.1 M MeOH accelerated the sulfoxide formation 10 times and *t*-BuOH 3 times. Quite interestingly, aprotic solvents such as DMF, DMSO, and HMPA caused a significant, i.e., ca. 3-fold, increase in chemical conversion. Although the effect of 0.1 M MeCN was not apparent, the reaction was 12 times faster in 50% MeCN and 19 times faster in 50% MeCN containing 0.1 M $Bu_4N{\cdot}ClO_4$. The effects of additives suggest that persulfoxide intermediates are stabilized not only by hydrogen bonding with protic solvents but also by coordination with solvents. Details on this point are noted in the Discussion.

On the contrary, the rates of sulfone formation were practically constant in the presence of various types of additives. Protic or coordinating solvents had no effect at all. The contrasting behavior toward additives suggests two separate pathways for the formation of sulfones and sulfoxides.

^{18}O-Tracer Study. ^{18}O-tracer experiments were carried out in order to differentiate two mechanisms, eqs 2 and eq 3, for the formation of sulfones. The results are listed in Table III.



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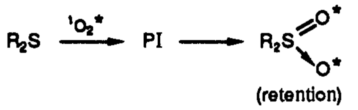

(3)

"Scramble" means that the two oxygens in sulfone are originated from two different O_2 molecules (eq 2). "Retention" means that sulfones are formed from one molecule of O_2 according to, for example, eq. 3. The data in Table III clearly show that the latter retention reaction is predominant (i.e., >90%), at least, for the initial stage of reaction. Even after 65% conversion in the $^1O_2$ reaction of 0.01 M **3f** in benzene (i.e., 59% PhSOMe and 6% $PhSO_2Me$), the retention pathway was 96% and again predominant. Thus, the major pathway for sulfone formation is the retention reaction as shown in eq 3.

Trapping 1 and 2. The effect of initial concentrations of sulfides on the product ratio R_2SO_2/R_2SO was examined for the $^1O_2$ reaction of **3a** in benzene. The reaction conditions were the same as those of Table I except for the concentrations of **3a**. The product ratios of R_2SO_2/R_2SO after 10 min of irradiation were practically constant, i.e., 0.36, 0.37, 0.33, and 0.35 with [**3a**] = 0.01, 0.05, 0.1, and 0.2 M, respectively. The constant formation of R_2SO_2 indicates that the PI intermediate to afford sulfones is not trapped by an excess amount of sulfides.

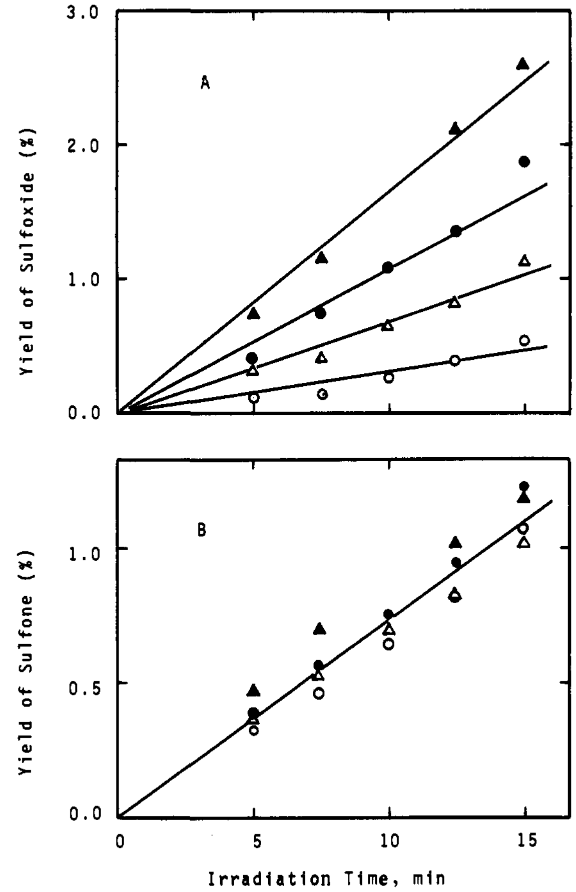

Figure 2. Effect of Ph_2SO on the $^1O_2$ reaction of 0.05 M **3a** in benzene. A and B are the time curves for the formation of sulfoxide and sulfone, respectively. Initial concentrations of Ph_2SO: (○), 0 M; (△), 0.05 M; (●), 0.10 M; (▲), 0.20 M.

The effect of diphenyl sulfoxide is quite interesting. As shown in Figure 2A, the sulfoxide formation is dependent on and increases with [Ph_2SO]. This means that the Ph_2SO trapping is competitive with the physical quenching (k_q). In sharp contrast, the sulfone formation is not affected at all by the presence of Ph_2SO (Figure 2B). This fact indicates that the PI intermediate to yield sulfones is not trapped by Ph_2SO. These experiments suggest the precursor to yield sulfones is not trapped by sulfides or sulfoxides. In other words, the unimolecular conversion to sulfones is very facile.

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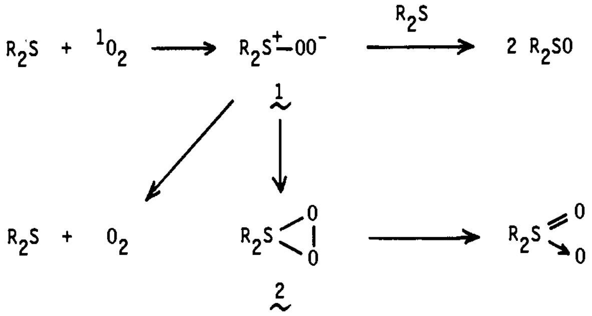
[22] The yield of sulfoxide was divided by a factor of 2 since one molecule of $^1O_2$ yields two molecules of sulfoxides.

Table IV. Temperature Effect on the $^1O_2$ Oxidation of **3a**[a]

temp (°C)	rel yield[b] (%)		E_a[c] (kcal/mol)	
	RSOR′	RSO$_2$R′	RSOR′	RSO$_2$R′
0[d]	8.0	0.63		
20	1.00[e]	1.00[e]	−9.9	+3.6
40	0.64	1.75		
60	0.25	1.97		

[a] Reaction of 0.05 M **3a** in benzene. See note *a* of Table II for conditions. [b] Relative yields were determined at the initial stage of reaction, i.e., 10 min of irradiation and below 10% conversion. [c] Apparent activation energy for the sulfoxide and sulfone formation as determined from Arrhenius-type plots of relative yields vs temperature. [d] The relative value at 0 °C was obtained in PhH/CH$_2$Cl$_2$ (9:1) in comparison to that at 20 °C. [e] The yields of sulfoxide and sulfone were 0.47 and 0.63%, respectively, by the irradiation of 10 min.

Scheme II



Temperature Effect. The temperature effect for the sulfoxide and sulfone formation is listed in Table IV. As reported previously,[17] the sulfoxide formation is favored at lower temperatures. The apparent activation energy estimated from the relative yields of sulfoxides is negative, i.e., −9.9 kcal/mol.

In contrast, the sulfone formation increased with temperatures, and the resulting activation energy is positive, i.e., +3.6 kcal/mol. As shown in the table, the sulfone formation becomes predominant at elevated temperatures; e.g., at 60 °C the ratio R_2SO_2:R_2SO = 89:11. These temperature effects also support two different pathways for the formation of R_2SO_2 and R_2SO.

Discussion

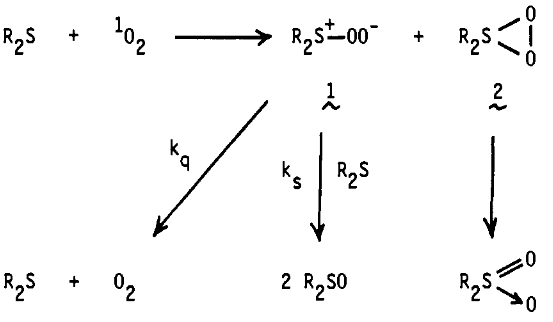
Persulfoxides (**1**) in the $^1O_2$ reaction of sulfides have been characterized by their reactivities[4,12,14,16] and direct observation.[15] Still unanswered is the intermediacy of cyclic thiadioxirane (**2**). We have noticed the sulfone formation as evidence for formation of **2**. The present results from the $^1O_2$ reaction of sulfides in aprotic solvents are summarized as follows: (1) Sulfone and sulfoxide formation are two major reactions. (2) Steric retardation by substituents is more significant for the formation of sulfone, while sulfoxide formation is more sensitive to the electronic effect. (3) Sulfoxide formation is accelerated significantly by protic and coordinating solvents, but sulfone formation is never affected by such additives. (4) ^{18}O-tracer experiments indicate that the two oxygen atoms in sulfones come from one oxygen molecule (i.e., the retention pathway). (5) The precursor for sulfones cannot be trapped by sulfoxides or sulfides. (6) The apparent activation energy for the sulfone formation is positive in contrast to the sulfoxide case. In the following, the intervention of **1** and **2** is discussed on the basis of these results.

Reaction Scheme. A consecutive sequence often written as eq 4 is not consistent with the decreasing ratio of R_2SO_2/R_2SO with increasing reaction times (Figure 1). ^{18}O-tracer experiments suggest that the retention pathway is predominant, eliminating eq 4 as the major pathway.

$$R_2S \xrightarrow{^1O_2} \underset{\mathbf{1}}{R_2S^+\text{–}O\text{–}O^-} \xrightarrow{R_2S} R_2SO \xrightarrow{1} R_2SO_2 \qquad (4)$$

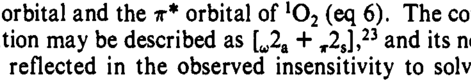
Also conceivable is Scheme II, which involves the conversion of persulfoxide (**1**) to thiadioxirane (**2**). This scheme is not consistent with the fact that the sulfone formation is unaffected by protic or coordinating solvents and by efficient trapping agents for **1** such as sulfoxides (Table II and Figure 2). According to Scheme II, the yields of sulfones should be reduced sharply by trapping **1**, which was not observed.

Scheme III



Scheme III is based on an assumption that **1** and **2** are formed as independent intermediates. All the results (1–6) summarized previously could be explained on the basis of this assumption. For example, the contrasting effects of additives and temperatures between the sulfone and sulfoxide formations are understood only by the assumption that sulfones and sulfoxides are obtained from two different reactions. The retention pathway by ^{18}O-tracer study is consistent with Scheme III. No effect of any additives in sulfone formation indicates that the cyclic intermediate **2** is facilely converted to sulfones.

Two reaction types for the formation of **1** and **2** are considered as eqs 5 and 6. Persulfoxides **1** are produced by the nucleophilic attack of lone-paired electrons of sulfur on the antibonding orbital of $^1O_2$ (eq 5). The formation of polar persulfoxides is supported by the observed large effect of solvents. The formation of cyclic **2** could be considered as a concerted cycloaddition between a sulfur lone pair orbital and the π^* orbital of $^1O_2$ (eq 6). The concerted cycloaddition may be described as $[_\omega 2_a + {}_\pi 2_s]$,[23] and its nonpolar nature is reflected in the observed insensitivity to solvents or additives. The more significant steric retardation for the sulfone formation may be understood by the crowded transition (**5**) in eq 6 compared with that of **4** in eq 5.



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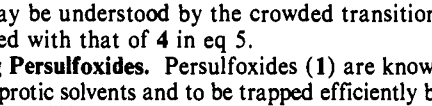
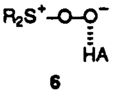


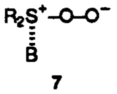
5 (6)

Stabilizing Persulfoxides. Persulfoxides (**1**) are known to be stabilized by protic solvents and to be trapped efficiently by other sulfide molecules.[4,16] The stabilization is based on the hydrogen bonding with protic solvent HA as depicted in **6**. Physical quenching to yield R_2S and O_2 becomes predominant in aprotic solvents because of the absence of hydrogen bonding.[16] However, the present study revealed that persulfoxides are stabilized also by coordinating solvents such as DMSO and DMF. This fact suggests that the stabilization through formation of **7** is significant and elogates the lifetime of **1** so as to react with another sulfide molecule (e.g., k_s in Scheme III). Alcohols may stabilize persulfoxides by hydrogen bonding (**6**) and also by coordination (**7**).



$$\underset{\vdots \atop HA}{R_2S^+\text{–}O\text{–}O^-}$$

6



$$\underset{\vdots \atop B}{R_2S^+\text{–}O\text{–}O^-}$$

7

The intervention of coordinated persulfoxide **7** is consistent with the following fact. In the $^1O_2$ reaction of 0.05 M **3a** in benzene,

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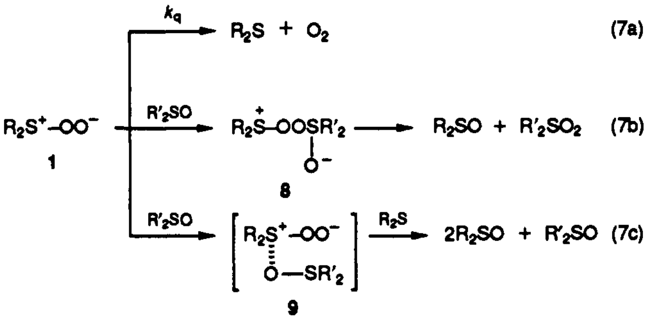
[23] See for notation: Woodward, R. B.; Hoffmann, R. In *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970; p 65.

the relative reactivities of di-*p*-tolyl sulfoxide/Ph_2S were 36, 27, and 18 in the presence of 0.0, 0.1, and 0.2 M PhSOMe, respectively. This could mean that the reactivity of **1** changes by the coordination of sulfoxides, i.e., B = R_2SO in **7**.[24] The intervention of **7** is in the same line with the recently reported result that the reaction of γ-hydroxy sulfides with $^1O_2$ proceeds via sulfurane intermediates involving the intramolecular hydroxyl group.[25]

Another factor in the stabilization of **1** is the effect of substituents. The relative rates for sulfoxide formation from thioanisoles are correlated with σ^+ to afford $\rho = -1.29$. The analysis of this substituent effect is somewhat complicated because the apparent data contains the effect for the oxidation of ArSMe by **1** (cf. k_s in Scheme III). In order to avoid the effect of the second step, the substituent effect for the $^1O_2$ oxidation of ArSMe was examined in the copresence of 0.5 M DMSO; DMSO was added to consume **1** effectively. The other conditions and method are the same as those of Table I. The resulting relative rates were 11.6, 1.00, 0.48, and 0.46 for substituents *p*-MeO, H, *p*-Cl, and *m*-Cl, respectively, affording the ρ-value of -1.28 (vs σ^+; $r = 0.98$).[26] It is interesting to note that the ρ-value for the reaction of **1** with DMSO is just the same as that with ArSMe (i.e., $\rho = -1.29$). This fact seems to suggest that the substituents effect in the oxidation step with **1** is of less importance. In other words, the apparent ρ-values reflect the stabilizing effect by substituents. The better correlation with σ^+ suggests the importance of electron-donating resonance in stabilizing persulfoxides.

Some consideration of Scheme I[16] is summarized in the following. An assumption that A and B are **1** and **2**, respectively, is denied as noted previously (cf. discussion on Scheme II). On the other hand, the reported interesting fact that the physical quenching via A is affected by the Ph_2SO but not by Ph_2S might be explained by the pathways 7a–c. That is, the physical quenching (eq 7a) is competitive with the nucleophilic oxidation of sulfoxides (**8** in eq 7b) and the coordination of sulfoxide oxygen to **1** (**9** in eq 7c). Scheme I might be explained if coordinated **9** could oxidize sulfides (eq 7c) but not sulfoxides. This seems to be supported by the fact that the sulfoxide formation was triplicated when DMSO was added (Table II). However, a more detailed trapping kinetics is necessary to support this assumption that A is free **1** and B is **9** in Scheme I.



Stability of Thiadioxiranes. The steady formation of sulfones unaffected by solvents or additives suggests that thiadioxirane (**2**) is formed in a different way from **1** and is facilely converted into sulfones. The facile conversion of **2** to sulfones is consistent with the retention pathway from $^{18}O_2$-tracer study and with no effect of added trapping agents.

The next question is whether thiadioxirane (**2**) is an intermediate or not. When our experimental approach was almost complete, a theoretical study[18] was published suggesting that cyclic thiadioxiranes exhibit no minimum on their potential energy surface. We reinvestigated the energy surface of **2** using HF/3-21G*, which consists of 3-21G and six d orbitals on O and S. Attempted calculations on C_{2v} or C_s potential energy surfaces did not afford any energy minimum for symmetric structure **10a** (R = H), as reported previously with 3-21G(*).[18] Then, we calculated an asymmetrical structure **10b** as four-coordinated sulfuranes and could find a stable cyclic structure as shown in Figure 3. The calculated thiadioxirane (**13**) possesses a bent sulfurane structure with apical oxygen (O_a) and hydrogen (H_a). It is interesting to note that the apical S–H_a bond is longer (1.363 Å) than the equatorial S–H_e bond (1.323 Å) and the S–O_a bond is longer (1.894 Å) than the S–O_e bond (1.541 Å). The angle ∠H_a–S–O_a of less than 180° and the ∠H_e–S–H_a of less than 120° are characteristic to most sulfuranes considered to have an equatorial lone pair.[27] Here, it should be remembered that a similar cyclic structure with an apical alkoxy group has been postulated to be involved in the reaction of sulfuranes with hydrogen peroxide.[28]

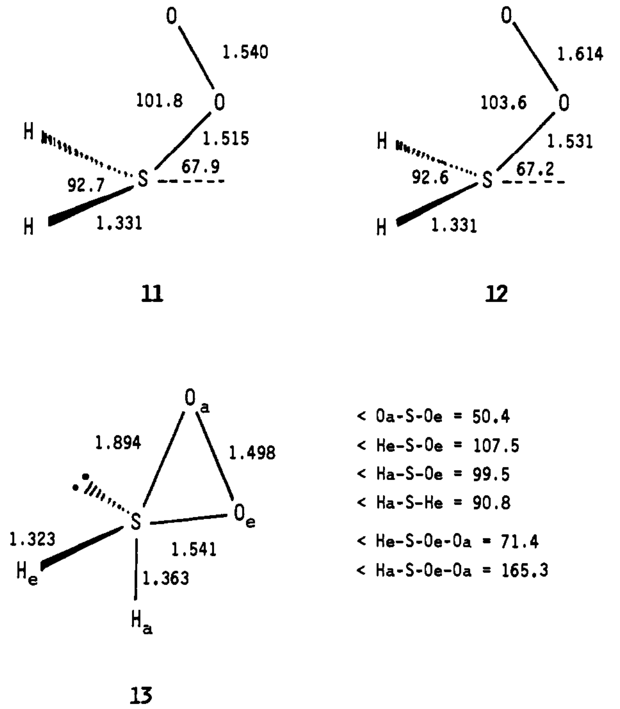
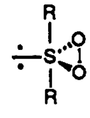
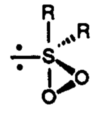


Figure 3. Optimized geometries of persulfoxide (**11**) and thiadioxirane (**13**) by HF/3-21G* and persulfoxide (**12**)[18] by HF/3-21G(*). Values in angstroms and degrees.



10a



10b

The total energy of thiadioxirane (**13**) is −544.546 77 au. Bent persulfoxide structure (**11**) calculated by HF/STO-3G* is close to the reported structure of **12**[18] by HF/STO-3G(*). The total energy of **13** is 3.3 kcal/mol more stable than the total energy of **11** (−545.541 51 au). The energy difference between **11** and **13** may be explained if it considered that sulfuranes having electronegative ligands at apical positions are known to be much more stable.[29] The calculated total energy of parent sulfone H_2SO_2 is −545.684 82 au, which is 86.6 kcal/mol more stable than thiadioxirane **13**. This explains the facile unimolecular conversion of **2** to sulfones and no observation of intermolecular trapping. These theoretical results suggest that thiadioxiranes are intermediates in the reaction of $^1O_2$ and sulfides and are converted facilely to sulfones.

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[24] Another possible case to cause the relative reactivity changing is such that only PhSOMe and di-*p*-tolyl sulfoxide are competing and Ph_2S is reacting with the other intermediate. To differentiate these possible pathways more detailed trapping experiments are required.

[25] Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044.

[26] The correlation with σ gave $\rho = -2.56$ with poorer correlation, $r = 0.85$.

[27] We acknowledge a reviewer who suggested these points on sulfurane structure.

[28] Martin, L. D.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *91*, 3511.

[29] Oae, S. *Organic Sulfur Chemistry*; Kagaku-dojin: Kyoto, 1982; Vol. I, 28.

Conclusion

Persulfoxides and thiadioxiranes are two important intermediates in the reaction of $^1O_2$ and sulfides. Dipolar persulfoxides are shown to be stabilized by hydrogen bonding and by coordination with solvents or additives. The formation of thiadioxiranes is not affected by solvents or additives, and the cyclic intermediates are facily converted to sulfones. A stable unsymmetrical structure is calculated for the thiadioxiranes.

Experimental Section

GC/MS spectra were recorded with a JEOL D300 mass spectrometer and ^1H NMR spectra with a Hitachi R24B spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph with 1- or 2-m columns: PEG 20M, 20% on Chromosorb WAW; Carbowax 300M, 20% on Chromosorb WAW; Porapack QS; Ultrabond PEG.

Materials. Sulfides (**3a**,**e**,**g**,**h**),[30] phenyl *tert*-butyl sulfide (**3d**),[31] and *p*-methylthioanisole (**3l**)[32] were prepared according to the reported methods and purified by distillation. Dibutyl sulfides (**3b**,**c**) and thioanisole (**3f**) were of commercial sources and of guaranteed grade. $^{18}O_2$ (99% pure) gas from CEA was diluted with O_2 gas. Solvent benzene was distilled before use. Other reagents and solvents were of commercial sources and used without further purification.

Typical Procedure of the Photooxidation. A 3-mL benzene solution of 0.05 M sulfides (**3**) and 0.1 mM tetraphenylporphin (TPP) in a 10-mL Pyrex test tube was purged with oxygen and irradiated at 20 ± 2 °C with a 300-W medium-pressure Hg lamp through a 5% $NaNO_2$ filter solution (i.e., ≥400 nm). The formation of sulfones and sulfoxides was determined at appropriate intervals of time by GLC with use of a 1-m column of PEG 20 M at 60–250 °C. The products were identified by GC/MS in comparison to authentic samples.

The relative rates for the $^1O_2$ oxidation of sulfides were determined from the times required for 1% conversion. Relative rates for the sulfoxide and sulfone formation were obtained from relative consumptions, and the resulting product ratios are as listed in the last two columns in Table I. The combined yields of sulfones and sulfoxides were ≥80% in benzene and ≥90% in acetonitrile. The accompanying minor reaction was the C–S cleavage to afford aldehydes; e.g., the yields of octanal from **3a** were 8 and 2% in benzene and acetonitrile, respectively. This minor reaction is not included in the Tables.

The effect of additives on the $^1O_2$ oxidation of **3a** were determined from the product yields after 10 min of irradiation of 0.05 M **3a** and 0.1 mM TPP in benzene. Two or three determinations were averaged, the resulting probable error being ±5%. The results are listed in Table II. The effect of temperature was examined at 0–60 °C in the $^1O_2$ oxidation of **3a**. A benzene solution of 0.05 M **3a** and 0.1 mM TPP was irradiated for 10 min, and the conversion of **3a** was determined by GLC. Two or three determinations were averaged, and the results are listed in Table IV.

Effect of Ph_2SO on the $^1O_2$ oxidation of **3a** was examined in the absence and presence of 0.05, 0.10, and 0.20 M Ph_2SO in benzene at 20 °C. Products were determined by GLC at appropriate intervals of time, and the results are shown in Figure 2.

The quantum yields for the sulfoxide and sulfone formation were determined by irradiation of 0.05 M **3a** and 0.1 mM TPP in benzene and MeOH/PhH (2:1) at >400 nm under oxygen. The light adsorbed was determined by use of the ferrioxalate actinometry.[33] Products were determined by GLC, and the yield of sulfoxide was divided by a factor of 2 since one molecule of $^1O_2$ produces 2 mol of sulfoxide.

^{18}O-Tracer Study. A 1-mL solution of 0.05 M thioanisole (**3f**) and 0.1 mM TPP was placed in a 5-mL test tube with a septum rubber cap. After the solution was purged with argon, oxygen gas ($^{32}O_2$:$^{34}O_2$:$^{36}O_2$ = 100:0.6:8.4) was introduced into the test tube through a syringe by exhausting the argon gas with another syringe. After irradiation of an appropriate time at ≥400 nm, the resulting reaction mixture was analyzed by GC–MS with a 1-m GC column of Ultrabond PEGS. For the case of thioanisole (**3f**), the mass spectral data around the parent peak (M) were easily obtained by a conventional EI method. In the case of octyl methyl sulfide (**3a**), MS analyses were carried out with a CI detector with methane gas.

The data in Table III summarize the mass spectral data obtained by three to five determinations. The contents of ^{18}O in RSO_2R were calculated from M + 2 and M + 4 values after abstracting those of natural abundance, as shown in parentheses in Table III, of authentic sulfones prepared from RSR′ and *m*-chloroperbenzoic acid. From the resulting M + 2 and M + 4 ratios as shown in brackets in Table III, the percent retentions were calculated as follows: Starting from $^{32}O_2$:$^{34}O_2$:$^{36}O_2$ = 100:0.6:8.4, the retention scheme for RSO_2R' leads to the M:(M + 2):(M + 4) ratio of 100:0.6:8.4, while the scrambling pathway results in the ratio of 100:16.8:0.7. When the ratio of retention and scrambling is f, the (M + 2)/(M + 4) ratios due to ^{18}O are expressed by eq 8. Thus, the values of f may be calculated from the (M + 2)/(M + 4) ratios obtained.

$$\frac{M + 2}{M + 4} = \frac{0.6f + 16.8}{8.4f + 0.7} \tag{8}$$

Theoretical Calculations. The calculations were carried out on HITAC M-680H and S-820/80 computers using a GAUSSIAN 82 program system.[34] The basis set consisted of 3-21G[35] and six d orbitals on S (radial exponent α = 0.65)[36] and O (α = 0.80).[37] The structures were optimized with the restricted HF (RHF) procedure by use of standard gradient techniques. The structures for thiadioxirane (**13**) and persulfoxide (**11**) are shown in Figure 3, the total energies being −545.546 77 and −545.541 51 au, respectively. The optimized structure of persulfoxide (**12**)[18] by HF/3-21G(*) is also shown in Figure 3 for comparison; the two structures are quite similar to each other. The parent sulfone, H_2SO_2, was calculated to be in C_{2v} structure; R(S–H) = 1.329 Å, R(S–O) = 1.420 Å; ∠H–S–H = 97.5°, ∠O–S–O = 123.0°; total energy = −545.684 82 au.

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