Substituent-Dictated Partitioning of Intermediates on the Sulfide Singlet Oxygen Reaction Surface. A New Mechanism for Oxidative C−S Bond Cleavage in α-Hydroperoxy Sulfides

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Abstract: The reactions of singlet oxygen with 17 sulfides bearing either anion or radical stabilizing substituents are reported. The abilities of substituents to modify product compositions in both the oxidative cleavage and sulfide oxidation pathways are analyzed in terms of partitioning of the hydroperoxy sulfonium ylide intermediate. Evidence is presented that suggests that the hydroperoxy sulfonium ylide exists in both diradical and zwitterionic forms. In addition, both inter- and intramolecular pathways for decomposition of α-hydroperoxy sulfides are suggested to rationalize the substituent-dependent formation of oxidative C−S bond cleavage products.

Introduction

The formation of sulfoxides and sulfones during the reactions of organic sulfides with singlet oxygen ($^1\Delta_g$) was first reported by Schenck and Krauch in 1962.[1] Remarkably, nearly 40 years after this seminal contribution there is still lack of a generally accepted description of the reaction surface for this deceptively simple process.[2] The focal point for the current debate is the identity of the second intermediate, **B**, on the Foote reaction surface.[3] (Scheme 1).

The kinetic evidence for two discrete intermediates was first presented by Foote and co-workers[3] in their now classic 1983 paper. In this same paper they suggested that the first intermediate, **A**, was a persulfoxide (or possibly an ion pair) and the second intermediate, **B**, a thiadioxirane.[4−8] This suggestion was based on the observations that **A** functions as a nucleophilic[9] and **B** as an electrophilic[10] oxygen transfer agent. Jensen[11] located both dimethylpersulfoxide and dimethylthiadioxirane on the MP2/6-31G* reaction surface ostensibly providing support for this assignment. However, as pointed out by Jensen, the two intermediates were separated by an activation energy barrier of nearly 20 kcal/mol inconsistent with the experimental facts.[12] Jensen also pointed out that a substantial body of experimental and theoretical evidence supported the persulfoxide as intermediate **A**, consequently implying that the thiadioxirane was not intermediate **B**.

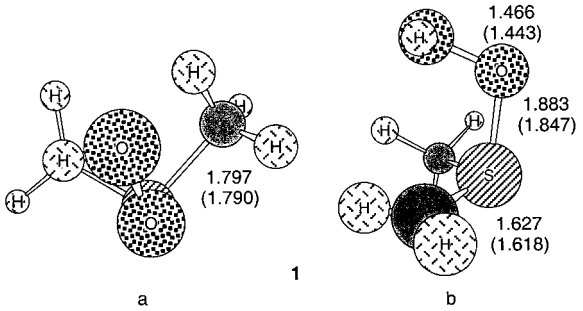
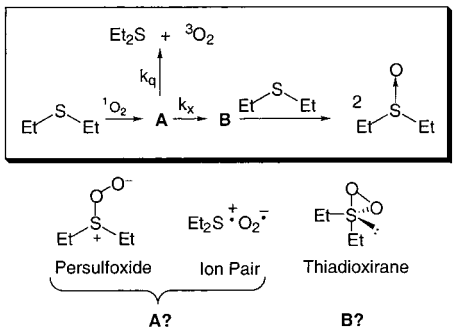


Figure 1. (a) Hydroperoxysulfonium ylide **1** looking down the O−S bond showing the O−O bond bisecting the C−S−C bond angle and the MP2/6-31G(d) and MP2/6-311+G(2df) (parentheses) S−CH_3 bond length. (b) Hydroperoxysulfonium ylide **1** looking down the H−O bond showing the planar CH_2 and the O−O, S−O, and S−CH_2 bond lengths.

Scheme 1



In 1998 Jensen and co-workers[12] on the basis of additional ab initio studies suggested a revised mechanism that invoked a hydroperoxy sulfonium ylide, **1** (Figure 1), as intermediate **B**. The hydroperoxy sulfonium ylide is formed at the CCSD(T)/6-31G(d) level by an intramolecular proton abstraction in the persulfoxide with an estimated barrier of 6 kcal/mol consistent

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(2) Ishiguro, K.; Sawaki, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 535−552.
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(5) Ando, W.; Takata, T. *Photooxidation of Sulfur Compounds*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. III, pp 1−117.
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(9) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947−5948.
(10) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191−194.
(11) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478−6487.
(12) A second transition structure connecting the persulfoxide and thiadioxirane was subsequently located which is only 11−13 kcal/mol above the persulfoxide, substantially more accessible but yet inconsistent with the experimental facts. Jensen, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* **1998**, *120*, 4439−4449.

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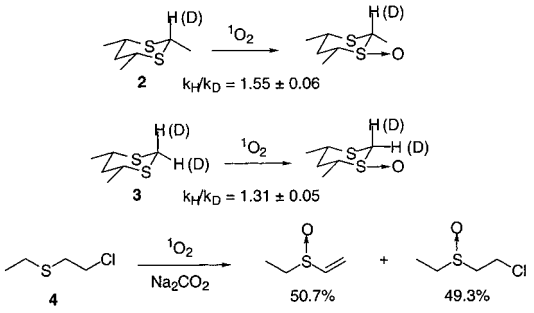
with experimental results which requires a rapid interconversion even at low temperatures. The minimum energy MP2/6-311+G-(2df) optimized geometry of the hydroperoxy sulfonium ylide is shown in Figure 1. The hydroperoxy sulfonium ylide has a short S−CH_2 bond indicative of double bond character and an O−O bond that bisects the C−S−C angle (Figure 1). The most stable conformation (Figure 1) has the peroxy hydrogen directly over the CH_2 at a distance of 3.15 Å. Three other conformations which were located do not have the peroxy hydrogen above the CH_2 group and are 1.5, 2.1, and 2.2 kcal/mol higher in energy, implying the existence of a hydrogen bond in **1** worth approximately 1 to 1.5 kcal/mol. The hydroperoxy sulfonium ylide had previously been suggested as a key intermediate in the oxidative cleavage of C−S bonds[13−16] and in sulfone formation.[17]

Compelling experimental evidence supporting the theoretical prediction of a hydroperoxy sulfonium ylide on the reaction path to sulfoxide has also been reported. In particular, photooxidations of 1,3-dithianes, **2** and **3**, and their 2-deuterated analogues, which react exclusively to give a single sulfoxide product, gave substantial isotope effects indicative of α-proton abstraction.[18] In addition, the formation of ethyl vinyl sulfide during photooxidation of 2-chloroethyl ethyl sulfide, **4**, can most easily be rationalized by invoking a *β*-elimination from a hydroperoxy sulfonium ylide intermediate.[19] On the other hand, Ishiguro et al.[17] have provided compelling evidence that the hydroperoxy sulfonium ylide, **1**, is on the reaction surface for sulfone formation. They have also provided experimental data that suggest that the sulfone and sulfoxide do not form from the same intermediate and that **1** is not an intermediate on the Foote (sulfoxide) reaction surface.



We report here the results of a study of the photooxidations of sulfides **5a**−**q** which bear a variety of radical and anion stabilizing substituents.[20] These new results provide fresh insight into the shape of the very complicated singlet oxygen−sulfide reaction surface. In particular, it provides very useful information about the environmental and structural features that determine the partitioning of the hydroperoxy sulfonium ylide, **1**, among the sulfoxide, sulfone, or oxidative cleavage (Pummerer rearrangement) reaction channels. In addition, the results from photooxidations of these substrates suggest that the cleavage reaction can occur via either radical- or anion-mediated Pummerer rearrangements and that the Pummerer product, the α-hydroperoxy sulfide, decomposes by both unimolecular and bimolecular processes.

Table 1. Product Ratios in the Room Temperature Photooxidations of **5**[a,b]

sulfide	SO	SO_2	R_2CO	ROOH	ROH	RSSR/RS(O)SR
5a	32	8	60			10/90
5b	47	17	36			28/72
5c	48		9		43	71/29[c]
						88/12[d]
5d	50	10	40			20/80
5e	41	9	50			12/88
5f	33		67			0/100
5g	37	11	52			100/0
5h	62	8	30			*e*
5i			100			33/67
5j			100			25/75
5k	23[f]		20[f]	57[f]		100/0[f]
	49[g]		51[g]			
5o	60	4	36			*h*
5q	41		35	24		100/0

[a] All photooxidations in $CDCl_3$ to approximately 20% conversion or less. The products are formed quantitatively with only traces of byproducts, except where noted, and material balances were >95% in all cases. Product ratios are the average of multiple determinations which were determined by ^1H NMR using in many, but not all, cases acetone or fluorene as internal standards. The product ratios are good to ±1−2%. [b] SO = sulfoxide; SO_2 = sulfone; R_2CO = carbonyl cleavage product; ROOH = α-hydroperoxy sulfide; ROH = α-hydroxy sulfide; RSSR = disulfide; RS(O)SR = thiolsulfinate. [c] 0.08 M **5c**. [d] 0.7 M **5c**. [e] Too complex for confident analysis. [f] Products detected immediately after photooxidation at 25 °C. [g] Products detected after sitting at room temperature for 24 h at 25 °C. [h] Not determined.

5

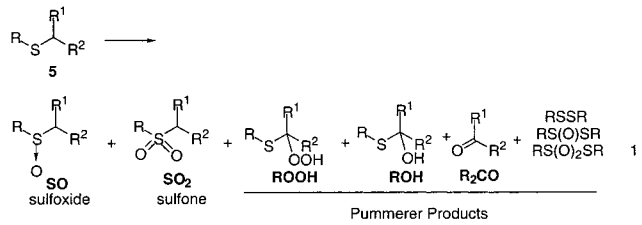
a. R = -CH_3; R^1 = H; R^2 = *trans*-CH=CHCO_2Et
b. R = -CH_3; R^1 = H; R^2 = -CH=CH_2
c. R = -CH_3; R^1 = H; R^2 = -CO_2Me
d. R = -CH_3; R^1 = H; R^2 = -C_6H_5
e. R = -Et; R^1 = H; R^2 = -C_6H_5
f. R = -Et; R^1 = H; R^2 = -SEt
g. R = -Et; R^1 = H; R^2 = -CO_2Et
h. R = -Et; R^1 = -CH_3; R^2 = -CO_2Me
i. R = -Et; R^1 = -SEt; R^2 = -COMe
j. R = -Et; R^1 = -SEt; R^2 = -CO_2Me
k. R = -C_6H_5; R^1 = H; R^2 = -CO_2Et
l. R = -C_6H_5; R^1 = H; R^2 = -CF_3
m. R = -C_6H_5; R^1 = H; R^2 = -$N^+(CH_3)_3$ ClO_4^-
n. R = -C_6H_5; R^1 = H; R^2 =  Cl^-
o. R = -C_6H_5; R^1 = H; R^2 = -COCH$_3$
p. R = -C_6H_5; R^1 = H; R^2 = -CON$(CH_3)_2$
q. R = tBu-; R^1 = H; R^2 = -CO_2Et

Results

The tetraphenylporphyrin (TPP) sensitized photooxidations of 0.05 to 0.13 M $CDCl_3$ solutions of **5a**−**q** were conducted by irradiations under a constant stream of O_2 with a 600 W tungsten lamp at 23 °C through 1 cm of a 12 M $NaNO_2$ solution filter. The reactions were monitored by ^1H NMR and the products isolated by chromatography and identified by spectroscopic comparison to independently synthesized materials (Table 1). To generate reproducible results it was necessary to protect the $CDCl_3$ from contact with the atmosphere by storage under nitrogen at 10 °C and to carefully remove residual acid by stirring the reaction mixtures with Na_2CO_3 prior to irradiation. Identical results were obtained in the reactions of 0.1 M solutions of the sulfides with 3 equiv of 1,4-dimethylnaphthalene endoperoxide providing evidence for the singlet oxygen origin of the products listed in Table 1. The product ratios are the average of 2 to 3 photooxidations and the product balances were measured in most cases by comparison to an internal standard and were greater than 95% in all cases. Control reactions also demonstrated that the product ratios were essentially independent of conversions between 20 and 70%.

(13) Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, 4263−4266.
(14) Ando, W.; Ito, K.; Takata, T. *Tetrahedron Lett.* **1982**, *23*, 3909−3912.
(15) Takata, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767−4770.
(16) Takata, T.; Ishibashi, K.; Ando, W. *Tetrahedron Lett.* **1985**, *26*, 4609−4612.
(17) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265−7271.
(18) Toutchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, *64*, 5620−5625.
(19) Toutchkine, A.; Clennan, E. L. *Tetrahedron Lett.* **1999**, *40*, 6519−6522.
(20) Toutchkine, A.; Clennan, E. L. *J. Am. Chem. Soc.* **2000**, *122*, 1834−1835.

All of the compounds with the exceptions of **5l**−**n** react with singlet oxygen to give a mixture of sulfoxides, sulfones, and Pummerer products (eq 1). The α-hydroperoxy sulfides (**ROOH**) serve as immediate precursors to the cleavage products. This suggestion is supported by careful monitoring of the photooxidation of **5c** by NMR. For example, in a sample of **5c** photooxidized to 9% conversion the reaction mixture consisted of 35% sulfoxide, **5-SO**, 12% carbonyl cleavage product, **5-R_2CO**, 19% α-hydroperoxy sulfide, **5-OOH**, and 34% α-hydroxy sulfide, **5-OH**. Within a few minutes (e.g. 20 min) at room temperature the α-hydroperoxy sulfide completely disappeared concomitant with formation of equal amounts of the α-hydroxy sulfide and the sulfoxide. This is followed by a much slower decomposition of the α-hydroxy sulfide to give the carbonyl cleavage product. NMR can also be used to demonstrate the formation of the α-hydroxy sulfides and cleavage products during the reactions of dimethyl sulfide with **5k-OOH**, **5p-OOH**, and **5q-OOH**. In the cases of **5k** and **5q**, which give the α-hydroperoxy sulfides exclusively at low temperatures, it can also be verified that the ratio (α-hydroxy sulfide + RSH)/Me_2SO is equal to 1 as required by the balanced equation RSCH(OOH)R′ + Me_2S → RSCH(OH)R′ + RSH + HCOR′ + Me_2SO.



The thiolsulfonates ($RS(O)_2SR$) become an increasingly important sulfur-containing cleavage product at higher conversions suggesting that they are products of over-photooxidation. The disulfide (RSSR) and thiolsulfinate (RS(O)SR), however, are primary products (vide infra) of α-hydroperoxy sulfide decomposition.

Disulfides are the predominant (≥60%) sulfur-containing cleavage product formed during phootooxidations of sulfides **5c**, **5g**, **5k**, and **5q.** Thiolsulfinates, on the other hand, are the predominant (≥60%) sulfur-containing cleavage products formed during photooxidations of sulfides **5a**, **5b**, **5d**, **5e**, **5f**, **5i**, and **5j**. These disulfide/thiolsulfinate ratios were reproducible if we treated our solvents carefully to remove trace acid, used low concentrations of starting materials (0.01 to 0.13 M), controlled conversions to 20% or less, and eliminated delays in the analysis of reaction mixtures.

Careful treatment of the reaction mixtures, as described earlier, minimized (and in some cases completely suppressed) thiolsulfinate disproportionation[21] and cleavage which could potentially obviate any mechanistic conclusions. Nevertheless, there seems to be a minor, and as yet unidentified, pathway early in the photooxidations that produce carbonyl cleavage products and thiolsulfinates (RS(O)SR). As a result the disulfide/thiolsulfinate ratio increases slightly with percent conversion. As pointed out earlier, however, the product ratios are nearly independent of conversions between 20% and 70%. In addition, this minor pathway appears to be suppressed, or less noticeable, when higher concentrations (>0.1 M) of substrates are used. We speculate, but have not unambiguously demonstrated, that this minor pathway, only observed at very low conversions, may be related to the presence of a minor amount of residual water that we have been unable to remove from the reaction mixtures.

(21) Kice, J. L. *Mechanisms and Reactivity in Reactions of Organic Oxyacids of Sulfur and their Anhydrides*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1980; Vol. 17, pp 65−181.

Table 2. Rate Constants for Sulfide ($PhSCH_2X$) Quenching of Singlet Oxygen

X	σ_I[a]	E_S[a]	$k_T \times 10^4$, M^{-1} s^{-1}
CH_3	0.01	−1.24	75.3
H	0	0	78.0
$CON(CH_3)_2$	0.28		25.0
CO_2Et	0.34		6.7
COMe	0.33		15.2
CF_3	0.38	−2.4	1.9
$N^+(CH_3)_3$	0.86	−2.84	0.65

[a] From ref 31.

Table 3. Low Temperature Photooxidations of Sulfides

sulfide	concn	*T* (°C)	**SO**	SO_2	R_2CO	**ROOH**
5e	0.03−0.06	23	41	9	50	
		0	61	9	30	
		−30	83	8	9	
		−42	75	21	4	
5f	0.03−0.06	23	33		67	
		0	55	10	45	
		−30	64	9	26	
		−42	73		18	
5h	0.05	23	62	8	30	
	0.04	0	63	6	31	
5k	0.06	25	23		20	57
	0.06	0				>95
	0.06	−30				>95
5o	0.01	−30	16		19	60
	0.07	−30	74		11	15
	0.13	−30	91		4	5
5p	0.03	−30	11	12	12	65
5q	0.05	23	41		35	24
	0.05	−30				>95

[a] For labels see footnote *b* in Table 1.

Compounds **5l**−**n** are deactivated toward reaction with singlet oxygen by potent electron withdrawing groups. The rate constants for substrate-induced removal of singlet oxygen, k_T, by **5l** and **5m** are 40 and 120 times smaller, respectively, than k_T for thioanisole (Table 2). The rate constants are linearly related ($\rho_I = -2.5$) to the inductive substituent constant, σ_I, with a modest correlation coefficient of 0.927, which can be improved to 0.966 when treated with a multiple regression analysis using both the inductive, σ_I, and steric parameter, E_S. The magnitudes of the reaction constants in the multiple regression analysis ($\rho_I = -1.6$, and $\rho_S = 0.34$) suggest that the inductive effect is more important that the steric effect in deactivating **5l**−**n**.

We have also examined the photooxidations of several sulfides, **5e**, **5f**, **5h**, **5k**, **5o**, **5p**, and **5q**, at low temperatures with the results given in Table 3. The extent of S−C bond cleavage decreases with temperature for the substrates with radical stabilizing substituents, **5e** and **5f**. In stark contrast, **5k** and **5q**, with anion stabilizing substituents, experience an increase in α-hydroperoxy sulfide formation with a decrease in temperature.

Discussion

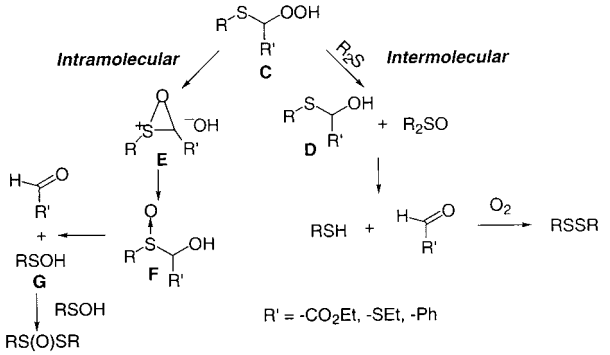
The two most important findings in this study are the following: (1) Sulfides **5c**, **5g**, **5k**, and **5q** react to give predominately disulfide sulfur containing (Pummerer) cleavage products while sulfides **5a**, **5b**, **5d**, **5e**, **5f**, **5i**, and **5j** react to give predominately thiolsulfinate cleavage products (Table 1) and (2) decreasing temperatures suppress formation of the

Table 4. Sulfide S-Oxidation/Pummerer Branching Ratios

>60% RS(O)SR		>60% RSSR	
sulfide	S-oxidation[a]/Pummerer[b]	sulfide	S-oxidation[a]/Pummerer[b]
5a	40/60	**5c**	48/52
5b	64/36	**5g**	49/52
5d	60/40	**5k**	49/51
5e	50/50	**5q**	41/55
5f	33/67		
5i	0/100		
5j	0/100		

[a] Sum of sulfoxide and sulfone products. [b] Carbonyl or α-hydroxy sulfide product.

Scheme 2

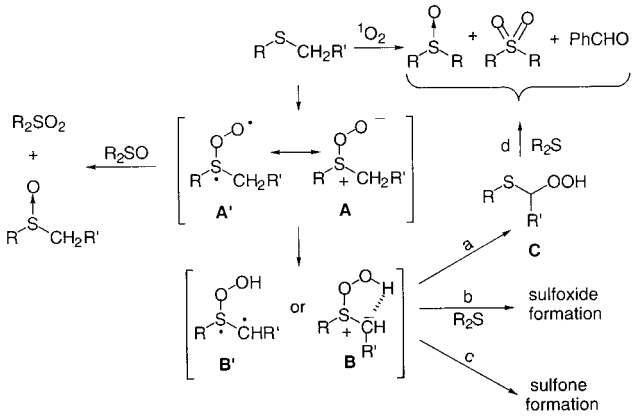


cleavage products during photooxidations of **5e** and **5f** with radical stabilizing substituents but enhance the formation of the cleavage products and/or their α-hydroperoxy sulfide precursors during photooxidations of sulfides with anion stabilizing substituents (Table 3). Both of these observations are analyzed in the following discussion and are used to construct a new detailed description of the sulfide photooxidation reaction surface.

Pummerer Cleavage Product Formation. Segregating the sulfides into two groups based upon their propensity to give predominately thiolsulfinate or disulfide cleavage products (Table 4) generates two distinctive sets of substrates. Those sulfides that give greater than 60% of the thiolsulfinate (RS(O)SR) all contain radical stabilizing substituents such as allyl (**5a** and **5b**), benzyl (**5d** and **5e**), and thioalkyl (**5f**), or captodatively synergistic groups (**5i** and **5j**). On the other hand, those sulfides that give greater than 60% of the disulfide (RSSR) cleavage product all contain an anion stabilizing carbonyl group (**5c**, **5g**, **5k**, and **5q**).

We suggest that this dichotomous formation of sulfide-containing cleavage products is indicative of two different mechanisms for the cleavage of the Pummerer rearrangement product, **C** (Scheme 2). The α-hydroperoxy sulfides **5c-OOH**, **5g-OOH**, **5k-OOH**, and **5q-OOH** with anion stabilizing substituents react via an intermolecular process involving reduction of the α-hydroperoxy sulfide with a molecule of starting material, formation of the α-hydroxy sulfide, **D**, cleavage to the thiol and carbonyl compound, and subsequent air oxidation of the thiol to the disulfide. This suggestion is supported by the direct observation of the α-hydroxy sulfide, **D**, during photooxidations of both **5c** and **5g**. Radical stabilizing substituents, on the other hand, direct cleavage via an intramolecular process that involves formation of an oxathiiranium ion, **E**, which, in analogy to thiiranium ions,[22] can collapse to a α-hydroxy sulfoxide, **F**, by hydroxide attack at either carbon or sulfur. The α-hydroxy sulfoxide decomposes to a sulfenic

Scheme 3



acid, **G**, and the carbonyl fragmentation product. The sulfenic acid can react either with another sulfenic acid to form its anhydride, the thiolsulfinate, or with a thiol formed in the intermolecular process to form the disulfide.[21]

The choice of reaction pathway appears to be dictated by the electronic character of the α-substituent. Radical stabilizing groups react via the entropically favored formation of the oxathiiranium ion. This route is so fast that in stark contrast to sulfides with anion stabilizing groups a hydroperoxy sulfide, **C**, bearing radical stabilizing groups is never directly observed. Electron withdrawing anion stabilizing groups, on the other hand, destabilize the oxathiiranium ion, **E**, and react preferentially via the intermolecular pathway. The photooxidations of **5i** and **5j**, however, appear to be exceptions to this generalization. These compounds give cleavage products but no sulfoxide (Table 1) and consequently must be reacting entirely by the intramolecular route. We suggest that the intramolecular decomposition of **5i-OOH**, and **5j-OOH**, despite the presence of the electron withdrawing carbonyl group, is understandable and is a direct result of the Thorpe−Ingold (gem-disubstituent) effect that promotes three-membered ring formation.[23]

The S-oxidation/Pummerer branching ratios (Table 4) for the sulfide photooxidations provide corroborating evidence for the operation of both inter- and intramolecular α-hydroperoxy sulfide decomposition. The intermolecular route (Scheme 2) requires that the S-oxidation/Pummerer ratio be exactly 1/1, precisely as observed, within experimental error, during photooxidations of **5c**, **5g**, **5k**, and **5q**. On the other hand, the intramolecular route does not involve reduction of the α-hydroperoxy sulfide with a molecule of sulfide substrate and should not generate any sulfoxide or sulfone product. Nevertheless, photooxidations of sulfides **5a**, **5b**, **5d**, **5e**, and **5f** do give variable amounts of sulfone and sulfoxide products. We point out, however, that this is a result of competitive S-oxidation via the Foote mechanism (Scheme 1). The anion stabilizing groups on **5c**, **5g**, **5k**, and **5q** enhance the Pummerer reaction to the exclusion of the Foote oxidation. The radical stabilizing substituents on **5a**, **5b**, **5d**, **5e**, and **5f**, however, do not promote the Pummerer rearrangement, and as a consequence allow Foote oxidation to compete.

Temperature Effects. Sulfides with radical stabilizing and anion stabilizing substituents exhibit diametrically opposed behaviors in response to changes in temperature. As the temperature decreases the Pummerer process (a in Scheme 3) becomes less important for substrates with radical stabilizing substituents but more important for substrates with anion

(22) Fachini, M.; Lucchini, V.; Modena, G.; Pasi, M.; Pasquato, L. *J. Am. Chem. Soc.* **1999**, *121*, 3944−3950.

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stabilizing substituents. This dramatically different temperature dependence can be rationalized if hydroperoxy sulfonium ylide formation can occur by two competitive pathways: hydrogen abstraction to give **B′** and proton transfer to give **B** (Scheme 3). We envision **B** and **B′** as isomers rather than resonance structures since they have distinctly different placements of the hydroperoxy proton. In addition, **B** is a 8-S-3 sulfuranyl species and **B′** a 9-S-3 hypervalent radical.[24] In the sulfide substrates **5a**−**q** both hydrogen abstraction and proton-transfer pathways are feasible since the persulfoxide can be depicted as either a zwitterion, **A**, or a diradical, **A′**, and is most likely a hybrid of these two limiting resonance forms.[11] We are not aware of any other system where hydrogen atom abstraction and proton transfer are competitive. The importance of 1,3-diradical canonical contributors to the wave functions of 1,3-dipoles, however, is well established.[25] The chemistry of persulfoxides is dominated by their nucleophilic oxygen donor character although the behavior of the persulfoxides formed during photooxidations of benzyl ethyl sulfides has recently been attributed to their diradical forms.[26,27]

(a) Sulfides with Radical Stabilizing Substituents. Hydroperoxy sulfonium ylide **B**, by virtue of its intramolecular hydrogen bond, is more stable than **B′** and in most circumstances would be expected to be formed preferentially. However, the presence of radical stabilizing substituents allows the formation of **B′** to compete. At low temperatures, where the more favorable entropy content ($-T\Delta S^{\ddagger}$) of the transition state for formation of the freely rotating diradical-hydroperoxy sulfonium ylide, **B′**, is of less importance relative to $\Delta H^{\ddagger}$ than at room temperature, the population of **B** is expected to increase. Hydroperoxy sulfonium ylide **B** with radical stabilizing substituents by virtue of its localized negative charge and relatively strong intramolecular hydrogen bond shows no proclivity toward Pummerer rearrangement (path a in Scheme 3) and as a result prefers sulfoxide formation (path b in Scheme 3). Consequently, this analysis suggests an increase in sulfoxide formation during the photooxidations of sulfides **5e** and **5f** as the temperature is lowered. Examination of the data in Table 3 demonstrates that this suggestion is realized. Sulfoxide formation during photooxidations of **5e** increases from 41% at 23 °C to 75% at −42 °C, and during the photooxidations of **5f** from 33% at 23 °C to 75% at −42 °C.

This analysis suggests that proton transfer, to give **B**, in persulfoxides bearing radical stabilizing substituents (e.g. **5e** and **5f**) generates exclusively the sulfide oxidation products (Scheme 4) while hydrogen abstraction, to give **B′**, leads exclusively to cleavage product formation. Under these circumstances k_{HA}/k_{PT} (defined in Scheme 4) can be calculated from the ratio of products and analysis of k_{HA}/k_{PT} using transition state theory will provide both $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}(\mathrm{HA}) - \Delta H^{\ddagger}(\mathrm{PT})$ and $\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}(\mathrm{HA}) - \Delta S^{\ddagger}(\mathrm{PT})$. These values for both **5e** and **5f** are given in Table 5 and the plots of $\ln(k_{HA}/k_{PT})$ versus $1/T$ in Figure 2. The remarkable linearity of these plots provides compelling evidence for the sulfide photooxidation mechanism as presented in Scheme 3. The exclusive formation of cleavage products from **B′** is perhaps not surprising. The dimethylhydroxysulfuranyl radical is known to have a very short lifetime limited by its dissociation into Me_2S and hydroxy radical.[28] This same dissociation in **B′** would produce the more stable hydroperoxy radical. Re-addition of the hydroperoxy radical to the α-carbon would generate the α-hydroperoxy sulfide **C**.

Scheme 4

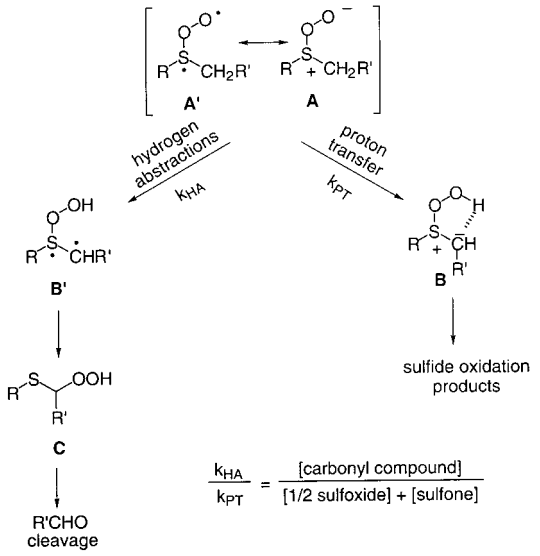

Table 5. Activation Barrier Differences for Hydrogen Transfer and Proton Transfer

compd	$\Delta\Delta H^{\ddagger}$ [a]	$\Delta\Delta S^{\ddagger}$ [b]
5e	6.8 ± 0.4	23.8 ± 1.6
5f	4.9 ± 0.4	19.0 ± 1.4

[a] $\Delta\Delta H^{\ddagger} = \Delta H_{HA}{}^{\ddagger} - \Delta H_{PT}{}^{\ddagger}$ in kcal/mol. [b] $\Delta\Delta S^{\ddagger} = \Delta S_{HA}{}^{\ddagger} - \Delta S_{PT}{}^{\ddagger}$ in eu.

The transition states for hydrogen abstraction to form **5e**-**B′** and **5f**-**B′** are energetically less accessible than the transition states for the proton transfer formation of **5e**-**B** and **5f**-**B** by 6.8 and 4.9 kcal/mol (Scheme 4 and Table 5). This is consistent with a substantial amount of the hydrogen bonding in **B** being present in the transition state for its formation. The hydrogen bond character in the transition states for formation of **5e**-**B** and **5f**-**B** also leads to substantially smaller entropy content than in the transitions states for hydrogen abstraction (column 3 in Table 5) as anticipated by the loss of rotational freedom in the hydrogen-bonded structure.

(b) Sulfides with Anion Stabilizing Substituents. The situation with the sulfides bearing anion stabilizing substituents is different. In these cases we suggest that only proton abstraction to form **B** (Scheme 3) is occurring. The negative charges in the zwitterionic hydroperoxy sulfonium ylides with anion stabilizing substituents, however, are extensively delocalized. This delocalization leads to a substantial weakening of the hydrogen bond depicted in **B** allowing the Pummerer (process a in Scheme 3) to occur with near exclusion of the competing processes b and c (Scheme 3). Consequently, the effect of decreasing temperatures in the reactions of **5k** and **5q** is to inhibit reduction of the α-hydroperoxy sulfide (path d in Scheme 3). For example, the α-hydroperoxy sulfide (ROOH) increases from 24% to greater than 95% during photooxidations of **5q** as the temperature is decreased from room temperature to −30 °C (Table 3).

Scheme 3 also predicts that at high sulfide (R_2S) concentration sulfoxide formation (path b in Scheme 3) should compete with the Pummerer rearrangement, path a. This is in fact observed

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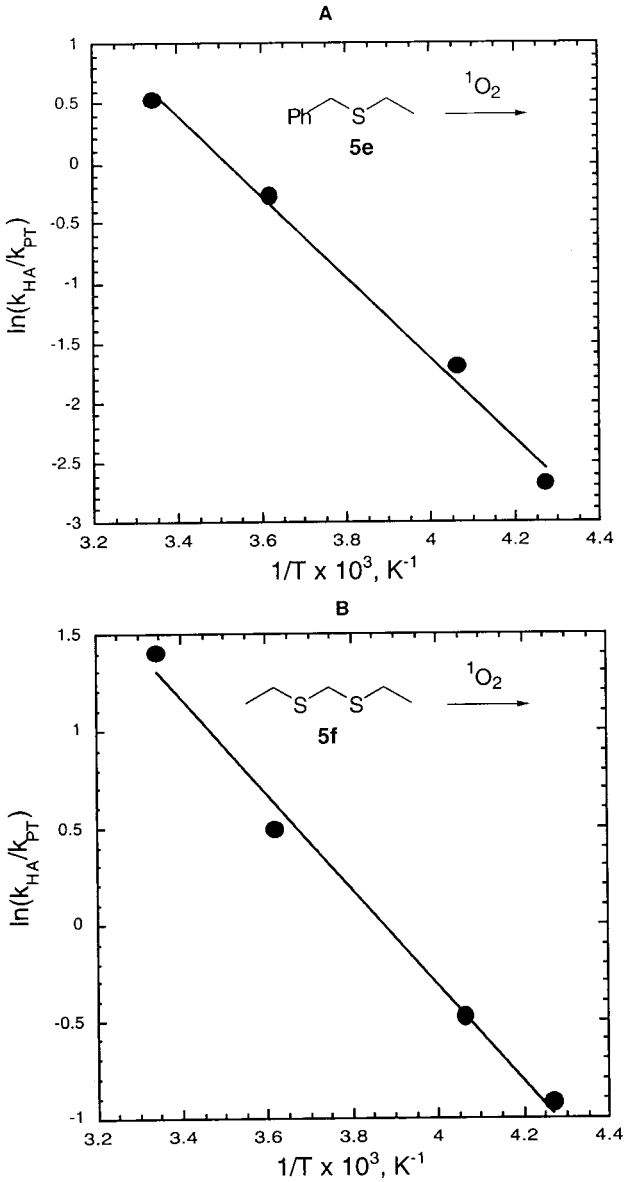
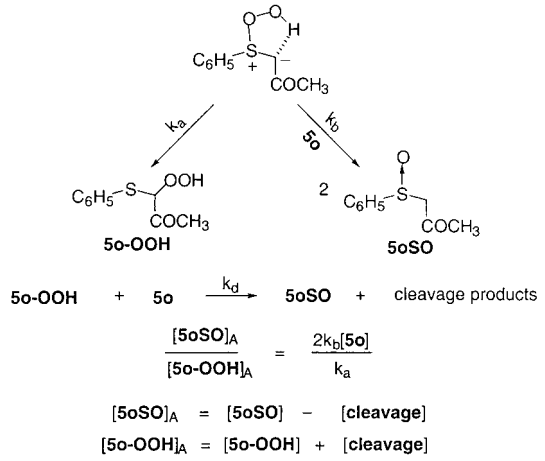


Figure 2. $\ln(k_{HA}/k_{PT})$ as defined in Scheme 4 versus $1/T$ for (a) **5e** and (b) **5f**.

during the photooxidation of the carboxy methyl substituted sulfide **5o** at −30 °C (Table 3). As the concentration of sulfide is increased from 0.01 to 0.13 M the sulfoxide yield increases from 16 to over 90% of the reaction mixture. This competition is described by the equations shown in Scheme 5. In this scheme $[\mathbf{5oSO}]_A$ is the concentration of the sulfoxide adjusted for sulfoxide produced during reduction of **5o-OOH** (process k_d), and $[\mathbf{5o\text{-}OOH}]_A$ is the concentration of the α-hydroperoxy sulfide adjusted for the amount lost in its reaction with **5o** (process k_d).[29] The analysis suggests that the second-order rate constant for sulfoxide formation (k_b) is approximately 40 times larger than the first-order rate constant for the Pummerer rearrangement (k_a). Consequently, the Pummerer rearrangement does not compete effectively with sulfoxide formation at typical substrate concentrations (0.05 to 0.2 M) in simple sulfides where the strength of the hydrogen bond in the hydroperoxy sulfonium ylide is more substantial than in **5o**.

(29) A plot of $[\mathbf{5oSO}]_A$ versus [**5o**] gives an intercept of −1.60, a slope of 80.45, and a correlation coefficient of 0.9607. At 0.01 M the sulfoxide yield was adjusted to 1% to complete the analysis. At 0.01 M $[\mathbf{5oSO}]_A/[\mathbf{5o\text{-}OOH}]_A$ = 1/79; at 0.07 M $[\mathbf{5oSO}]_A/[\mathbf{5OOH}]_A$ = 63/26; at 0.13M $[\mathbf{5oSO}]_A/[\mathbf{5OOH}]_A$ = 87/9.

Scheme 5



A high level ab initio computational study provides corroborating evidence for this new Pummerer rearrangement mechanism.[12] The lowest energy conformer of dimethylhydroperoxy sulfonium ylide was located and shown to adopt a hydrogen-bonded structure with a O−H−α-carbon distance of 3.15 Å at the MP2/6-311+G(2df) computational level.[12] In addition, a transition state connecting the hydroperoxy sulfonium ylide, **B**, to the α-hydroperoxy sulfide, **C**, was located.

Conclusion

Structural effects on the distribution of Pummerer, sulfoxide, and sulfone products formed during sulfide photooxidations are profound. Much of the complexity of this fascinating reaction can be traced to the mechanistic choices available to the second (electrophilic) intermediate formed on the Foote reaction surface. (Scheme 1) The experimental and computational results argue that this second intermediate is best described as a hydroperoxy sulfonium ylide (Figure 1). We have pointed out in this study that this second intermediate can also exist as either a closed intramolecularly hydrogen bonded or as an open freely rotating isomer. These isomers exhibit distinct reactivity as determined by their partitioning among the three available reactions channels (path a, b, and c in Scheme 3). Furthermore, the populations of these isomers in any given photooxidation are dictated by substituent effects and temperature.

Structural effects on the distribution of the S−C cleavage products are also profound. We have suggested that these product distributions can be understood if decomposition of the initial Pummerer product, the α-hydroperoxy sulfide (**C** in Scheme 2), occurs via competing inter- and intramolecular pathways. The structural effect on product distribution can be traced to the energetics of formation of a key oxathiiranium ion (**E** in Scheme 2), in the entropically favored intramolecular route. The stability of this intermediate is dramatically influenced by both the electronic and steric character of the substituents on both the sulfur and α-carbon atom in the sulfide substrate.

In conclusion, the use of substituent effects has proven to be a powerful tool for probing the very complicated sulfide photooxidation reaction surface. Particularly noteworthy is the ability of substituents to direct sulfide photooxidations exclusively along the Pummerer reaction surface. With the new data generated from an analysis of these substituent effects a detailed reaction surface that provides a rationale for the complicated reaction mixtures formed in these extremely important reactions is beginning to emerge.

Experimental Section

General Aspects. A HP-5 (30 m × 0.25 mm × 0.25 μm (length × inside diameter × film thickness)) capillary column was used for GC/MS data collection and a 5% diphenyl−95% dimethyl polysiloxane (30 m × 0.32 mm × 1.0 μm (length × inside diameter × film thickness)) or a HP-1 cross linked methyl silicon (30 m × 0.53 mm × 1.5 μm (length × inside diameter × film thickness)) fused silica column was used for analytical GC data collection. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ or C_6D_6 solutions of substrates and reaction mixtures were recorded at 400.13 MHz on a Bruker Avance DRX-400 spectrometer. The peaks corresponding to the residual protons of $CDCl_3$ (7.27 ppm) or C_6D_6 (7.16 ppm) were used as the internal reference. The triplet at 77.23 ($CDCl_3$) was used as the reference for the ^{13}C NMR spectra. Combustion analyses were obtained from Atlantic Microlab in Norcross, Georgia. Anhydrous diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl.

The endoperoxide of 1,4-dimethylnaphthalene was prepared by the method of Wasserman and Larsen.[30] 1,1-Dichloroacetone, thiophenol, thionyl chloride, and iodomethane were obtained from Acros Chemical and used without further purification. 1-Bromo-2,2,2-trifluoroethane, MCBPA, dimethylamine, ethyl *trans*-crotonate, *N*-bromosuccinimide, methanethiol, and benzyl mercaptan were obtained from Aldrich Chemical Co. and used without further purification. Anhydrous $MgSO_4$, pyridine (HPLC grade), and potassium carbonate were obtained from Spectrum and used without further purification.

One-hundred gram bottle(s) of chloroform-*d* (Cambridge Isotope Laboratories) were extracted with 40 mL of saturated aqueous sodium bicarbonate, dried with magnesium sulfate, and stored over 4 Å molecular sieves under nitrogen at 10 °C.

General Procedure for Sulfide Photooxidation. Photooxidation reaction mixtures 0.05−0.08 M in sulfide and 2.5 × 10^{-4} M in tetraphenylporphyrin (TPP) were prepared in $CDCl_3$ in 5 mL volumetric flasks. Each mixture was then treated with 0.25 g of Na_2CO_3 and allowed to stir for 10 min in the dark. The solutions were then filtered and divided into 1 mL portions for irradiation in 100 mL test tubes. The samples were presaturated with oxygen for 2 min and then irradiated under a constant stream of oxygen with a 600 W tungsten lamp at 23 °C through 1 cm of a 12 M $NaNO_2$ filter solution. The irradiation time is chosen to keep the conversion of starting material to less than or equal to 20%. After the photooxidations the samples are kept in the dark and analyzed by ^{1}H NMR as quickly as possible (5−10 min after photooxidation). The product ratios represent the averages from 3 to 4 independently photooxidized samples.

Ethyl γ-Methylthiocrotonate (5a). Ethyl *trans*-crotonate (10 g, 88 mmol) was stirred at reflux with 1 equiv of *N*-bromosuccinimide (NBS; 15 g) and 0.12 g of benzoylperoxide in 54 mL of carbon tetrachloride. The extent of bromination was monitored by gas chromatography. Additional NBS was added as necessary to bring the yield of the allylic bromide up to greater than 80%. The ethyl γ-bromo-*trans*-crotonate product was then purified by distillation. A portion of the allylic bromide (4.4 g; 23 mmol) was then added to 20 mL of diethyl ether and cooled to −78 °C. This solution was then treated with 0.9 equiv (1.0 g) of methanethiol and allowed to warm slowly to 0 °C. The reaction mixture was then treated with 0.9 equiv of triethylamine, stirred for 2 h, and finally heated at reflux for 4 h. The reaction mixture was worked up by washing with 30 mL of diethyl ether, drying with $MgSO_4$, and removal of diethyl ether by rotorary evaporation. Final purification was accomplished by radial chromatography (hexane/ethyl acetate 200/1) to give a 31% yield of product. ^{1}H NMR ($CDCl_3$) δ 1.3 (t, J = 7.1 Hz, 3H), 2.03 (s, 3H), 3.19 (dd, J = 7.5, 1.1 Hz, 2H), 4.2 (q, J = 7.1 Hz, 2H), 5.8(d, J = 15.5 Hz, 1H), 6.86 (dt, J = 15.5, 7.5 Hz, 1H).

Ethyl γ-Methylsulfinylcrotonate (5a-SO). ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 2.61 (s, 3H), 3.55 (ddd, J = 12.9, 7.9, 1.1 Hz, 1H), 3.62 (ddd, J = 12.9, 7.9, 1.1 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 6.11(bd, J = 15.6 Hz, 1H), 6.95 (dt, J = 15.6, 7.9 Hz, 1H).

Ethyl γ-Methylsulfonylcrotonate (5a-SO$_2$). ^{1}H NMR ($CDCl_3$) δ 1.30 (t, J = 7.3 Hz, 3H), 2.92 (s, 3H), 3.87 (d, J = 7.9 Hz, 2H), 4.24 (q, J = 7.3 Hz, 2H), 6.16 (d, J = 15.6 Hz, 1H), 6.95 (dt, J = 15.6, 7.9 Hz, 1H).

Methyl Thiomethyl Acetate (5c). ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 3.21 (s, 2H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 16.6, 35.7, 52.6, 171.0.

Methyl Methylsulfinyl Acetate (5c-SO). ^{1}H NMR ($CDCl_3$) δ 2.76 (s, 3H), 3.70 (d, J = 14 Hz, 1H), 3.74 (d, J = 14 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 39.7, 53.1, 57.8, 165.6.

Methyl Hydroxymethylthioacetate (5c-OH). ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 3.86 (s, 3H), 5.23 (d, J = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 11.7, 53.3, 73.8, 171.7.

Benzyl Methyl Sulfide (5d). Benzyl mercaptan (5.4 g, 43 mmol) was converted to the sodium thiolate by stirring with 1 equiv of sodium methoxide in 30 mL of methanol under a nitrogen atmosphere. Iodomethane (6.2 g, 44 mmol) was added dropwise to the methanol solution of the thiolate and the reaction mixture was refluxed overnight. The product was obtained in 82% yield after purification by distillation. ^{1}H NMR ($CDCl_3$) δ 1.99 (s, 3H), 3.68 (s, 2H), 7.23−7.34 (m, 5H).

Benzyl Methyl Sulfoxide (5d-SO). ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.93 (d, J = 12.8 Hz, 1H), 4.07 (d, J = 12.8 Hz, 1H), 7.23−7.34 (m, 5H).

Benzyl Methyl Sulfone (5d-SO$_2$). ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 3H), 4.25 (s, 2H), 7.23−7.34 (m, 5H).

Benzyl Ethyl Sulfoxide (5e-SO). ^{1}H NMR (C_6D_6) δ 0.91 (t, J = 7.5 Hz, 3H), 1.73 (dq, J = 13.1, 7.5 Hz, 1H), 2.03 (dq, J = 13.1, 7.5 Hz, 1H), 3.40 (d, J = 12.8 Hz, 1H), 3.48 (d, J = 12.8 Hz, 1H), 6.95−7.11 (m, 5H).

Benzyl Ethyl Sulfone (5e-SO$_2$). ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.5 Hz, 3H), 2.85 (q, J = 7.5 Hz, 2H), 4.22 (s, 2H), 7.4 (s, 5H).

Ethylthioethylmethyl Sulfide (5f). ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.4 Hz, 6H), 2.65 (q, J = 7.4 Hz, 4H), 3.69 (s, 2H).

Ethylthioethylmethyl Sulfoxide (5f-SO). ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.5 Hz, 3H), 1.31 (t, J = 7.5 Hz, 3H), 2.67−2.79 (m, 3H), 2.94 (dq, J = 13.3, 7.6 Hz, 1H), 3.64 (d, J = 13.7 Hz, 1H), 3.68 (d, J = 13.7 Hz, 1H).

Ethylthioethylmethyl Sulfone (5f-SO$_2$). ^{1}H NMR ($CDCl_3$) δ 1.29 (t, J = 7.5 Hz, 3H), 1.38 (t, J = 7.5 Hz, 3H), 2.90 (q, J = 7.5 Hz, 2H), 3.21 (q, J = 7.5 Hz, 2H), 3.82 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 6.72, 14.12, 27.09, 44.23, 51.28.

Ethyl Thioethyl Acetate (5g). ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.3 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 2.65 (q, J = 7.3 Hz, 2H), 3.17 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H).

Ethyl Ethylsulfinyl Acetate (5g-SO). ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.4 Hz, 3H), 2.82 (dq, J = 7.6, 13.6 Hz, 1H), 2.91 (dq, J = 13.6, 7.5 Hz, 1H), 3.64 (s, 2H), 4.22(q, J = 7.2 Hz, 2H).

Ethyl Ethylsulfonyl Acetate (5g-SO$_2$). ^{1}H NMR ($CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 1.43 (t, J = 7.4 Hz, 3H), 3.28 (q, J = 7.4 Hz, 2H), 3.94 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H).

Methyl 2-Thioethylpropionate (5h). ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.4 Hz, 3H), 1.41 (d, J = 7.1 Hz, 3H), 2.58 (dq, J = 12.4, 7.3 Hz, 1H), 2.62 (dq, J = 12.4, 7.4 Hz, 1H), 3.39 (q, J = 7.1 Hz, 1H), 3.70 (s, 3H).

Methyl 2-Ethylsulfinylpropionate (5h-SO). Two diastereomers. ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 1.39 (d, J = 7.1 Hz, 3H), 1.41 (d, J = 7.3 Hz, 3H), 2.62−2.70 (m, 4H), 3.45 (q, J = 7.1 Hz, 1H), 3.59 (q, J = 7.3 Hz, 1H), 3.65 (s, 3H), 3.66 (s, 3H)). ^{13}C NMR ($CDCl_3$) δ 6.79, 7.21, 9.50, 10.32, 42.73, 44.53, 52.59, 52.68, 58.44, 59.37, 168.39, 169.34.

Methyl 2-Ethylsulfonylpropionate (5hSO$_2$). ^{1}H NMR ($CDCl_3$) δ 1.42 (t, J = 7.4 Hz, 3H), 1.41 (d, J = 7.1 Hz, 3H), 3.17 (dq, J = 7.5, 13.9 Hz, 1H), 3.25 (dq, J = 7.5, 13.8 Hz, 1H), 3.81 (s, 3H), 3.94 (q, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 6.11, 10.65, 45.91, 53.53, 62.18, 167.34.

Pyruvaldehyde Diethylthioacetal (5i). Fifty millimoles of 1,1-dichloroacetone was added dropwise to a 50 mL slurry of dried acetone containing 5 g of powdered potassium carbonate and 120 mmol of ethyl mercaptan. The reaction mixture was allowed to stir at room temperature for 24 h and the dithioacetal isolated (6.8 g, 93% yield) by vacuum distillation as a slightly yellow oil (bp 138−139 °C; 0.7 mmHg). ^{1}H

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NMR ($CDCl_3$) δ 1.21 (t, $J = 7.4$ Hz, 6H), 2.32 (s, 3H), 2.53 (dq, $J = 12.6$, 7.4 Hz, 2H), 2.61 (dq, $J = 12.6$, 7.4 Hz, 2H), 4.34 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.35, 25.01, 25.85, 58.06, 201.10. Anal. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91. Found: C, 47.12; H, 7.80.

Methyl (Bisthioethyl)acetate (5j). Dithioacetal of methylglyoxate**.** 1,1-Dichloroacetone (0.05 mol) was added to a stirred suspension of 0.12 mol of anhydrous K_2CO_3 and 0.1 mole of ethyl mercaptan in dried acetone. This reaction mixture was allowed to stir for 24 h under a nitrogen atmosphere at room temperature. The resulting solid was filtered, the solvent evaporated, and the dithioacetal purified by vacuum distillation. ^{1}H NMR ($CDCl_3$) δ 1.26 (t, $J = 7.5$ Hz, 6H), 2.68 (dq, $J = 12.5$, 7.3 Hz, 2H), 2.75 (dq, $J = 12.6$, 7.5 Hz, 2H), 3.77 (s, 3H), 4.37 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.35, 25.34, 50.30, 53.09, 170.13. Anal. Calcd for $C_7H_{14}O_2S_2$: C, 43.27; H, 7.26. Found: C, 43.40; H, 7.20.

Ethyl Thiophenylacetate (5k). ^{1}H NMR ($CDCl_3$) δ 1.22 (t, $J = 7.1$ Hz, 3H), 3.63 (s, 2H), 4.16 (q, $J = 7.2$ Hz, 2H), 7.23−7.43 (m, 5H).

Ethyl Phenylsulfinyl Acetate (5k-SO). ^{1}H NMR ($CDCl_3$) δ 1.16 (t, $J = 7.2$ Hz, 3H), 3.64 (d, $J = 13.6$ Hz, 1H), 3.81 (d, $J = 13.6$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 3H), 7.49−7.66 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 14.08, 61.75, 62.08, 124.26, 129.46, 131.85, 143.15, 164.78.

Ethyl Phenylsulfonyl Acetate (5k-SO_2). ^{1}H NMR ($CDCl_3$) δ 1.19 (t, $J = 7.2$ Hz, 3H), 4.12 (s, 2H), 4.13 (q, $J = 7.2$ Hz, 2H), 7.56−7.96 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 13.77, 60.92, 62.33, 128.47, 129.13, 134.21, 138.59, 162.25.

Ethyl 2-Hydroperoxy-2-thiophenylethanoate (5k-OOH). ^{1}H NMR ($CDCl_3$) δ 1.28 (t, $J = 7.1$ Hz, 3H), 4.23 (q, $J = 7.1$ Hz, 2H), 5.68 (s, 1H), 7.36−7.60 (m, 5H), 9.54 (bs, 1H).

2,2,2-Trifluoroethyl Phenyl Sulfide (5l). Ten milliliters of ethanol containing 0.03 mol of 1-bromo-2,2,2-trifluoroethane was added dropwise at 0−5 °C to a stirred solution of 0.03 mol of sodium thiophenolate in 30 mL of ethanol. After the addition was complete the reaction mixture was allowed to stir for 24 h. The solid was filter off and the solvent was evaporated in a vacuum. Distillation of the residue gave 3.23 g (56% yield) of the pure sulfide as a colorless liquid (bp 90−92 °C; 15 mmHg). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 3.45 (q, $^3J = 9.7$ Hz, 2H), 7.31−7.51 (m, 5H).

***N,N,N*-Trimethylaminomethyl Phenyl Sulfide Perchlorate (5m).** A solution of 4.77 g (0.03 mol) of chloromethylphenyl sulfide in 100 mL of dry benzene was placed in a 250 mL two-neck round-bottom flask equipped with a gas inlet tube and a dry ice condenser. The mixture was stirred and heated to boiling at which point a stream of dry trimethylamine (ca. 0.05 mol) was passed through the solution. After the addition was complete the reaction mixture was allowed to reflux and stir for an additional 3 h. The solid $PhSCH_2N(CH_3)_3^+$ Cl^- was filtered and air dried. The yield was 5.12 g (78%). This salt was then converted to the perchlorate salt without further purification by ion exchange with silver perchlorate in water. The perchlorate salt was isolated by filtration, dried in a vacuum, and recrystallized from acetone/chloroform (1/2) to give 3.95 g (70% yield) of white crystals. ^{1}H NMR (400.13 MHz, CD_3COCD_3) δ 3.30 (s, 9H), 5.21 (s, 2H), 7.43−7.75 (m, 5H). Anal. Calcd for $C_{10}H_{16}O_4NSCl$: C, 42.63; H, 5.72. Found: C, 42.56; H, 5.76.

Pyridiniummethyl Phenyl Sulfide Chloride Monohydrate (5n). A solution of 4.77 g (0.02 mol) of chloromethyl phenyl sulfide and 1.65 g of dry pyridine in 100 mL of benzene was allowed to reflux for 12 h. The solvent was then evaporated in a vacuum and the residue recrystallized from acetone−ethyl alcohol−water (20:6:1) to give colorless crystals of the monohydrate. The anhydrous salt was obtained by drying in a vacuum (1 mmHg) for 12 h at room temperature. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 3.32 (s, 2H, H_2O), 6.57 (s, 2H), 7.24−7.39 (m, 5H), 7.94 (t, $^3J = 6.8$ Hz, 2H), 8.44 (t, $^3J = 6.8$ Hz, 1H), 9.23 (d, $^3J = 6.8$ Hz, 2H). Anal. Calcd for $C_{12}H_{12}NSCl$: C, 60.62; H, 5.09. Found: C, 58.81; H, 5.21.

1-Phenylthio-2-propanone (5o). Chloroacetone (0.05 mol) was added dropwise to a stirred suspension of potassium carbonate (anhydrous powder, 0.06 mol) and 0.05 mol of thiophenol in dry acetone. The reaction mixture was allowed to stir under a nitrogen atmosphere for an additional 6 h at room temperature after the addition of chloroacetone was complete. The solution was then filtered to remove a solid and the solvent was removed to give a residue that was distilled in a vacuum to give 5.60 g (68% yield) of a colorless liquid, which solidified upon standing in the refrigerator. The solid was recrystallized from petroleum ether−diethyl ether (7:3) to give colorless prisms (mp 35−36.5 °C). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.67 (s, 2H), 7.21−7.35 (m, 5H).

1-Phenylsulfinyl-2-propanone (5o-SO). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.24 (s, 3H), 3.81 (d, $J = 13.7$ Hz, 1H), 3.89 (d, $J = 13.7$ Hz, 1H), 7.26−7.67 (m, 5H).

1-Hydroperoxy-1-thiophenyl-2-propanone (5o-OOH). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.34 (s, 3H), 5.64 (s, 1H), 7.34−7.53 (m, 5H), 9.34 (bs, 1H).

***N,N*-dimethylthiophenylethanamide (5p).** (Phenylthio)acetic acid (5.04 g, 0.03 mol) was converted to the acid chloride by adding 15 mL of thionyl chloride and stirring for 30 min. The excess thionyl chloride was then removed in a vacuum and the residue dissolved in 50 mL of dry benzene. This solution was then placed in a 100 mL flask equipped with a reflux condensor, gas inlet tube, and a magnetic stirring bar. A slow stream of approximately 0.08 mol of dimethylamine was passed through the solution during a period of 15 min. This solution was then allowed to reflux and after cooling washed with water (2 × 20 mL) and dried with $MgSO_4$. The residue was distilled to give pure product (bp 153−155 °C; 1 mmHg). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.87 (s, 3H), 2.94 (s, 3H), 3.69 (s, 2H), 7.14−7.39 (m, 5H).

***N,N*-Dimethylphenylsulfinylethanamide (5p-SO).** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 2.84(s, 6H), 3.63(d, $J = 134.7$ Hz, 1H), 3.95(d, $J = 13.7$ Hz, 1H), 7.42−7.65(m, 5H). Anal. Calcd for $C_{10}H_{13}O_2NS$: C, 56.85; H, 6.20. Found: C, 56.31; H, 6.22.

Ethyl Thio-*tert*-butyl Acetate (5q). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.27 (t, $J = 7.2$ Hz, 3H), 1.33 (s, 9H), 3.28 (s, 2H), 4.18 (q, $J = 7.2$ Hz, 2H).

Ethyl *tert*-Butylsulfinyl Acetate (5q-SO). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.19 (s, 9H), 1.22 (t, $J = 7.2$ Hz, 3H), 3.28 (d, $J = 13.6$ Hz, 1H), 3.43 (d, $J = 13.6$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.08, 22.66, 51.67, 54.24, 62.10, 166.34.

Ethyl *tert*-Butylsulfonyl Acetate (5q-SO_2). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.32 (t, $J = 7.2$ Hz, 3H), 1.45 (s, 9H), 3.95 (s, 2H), 4.28 (q, $J = 7.2$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.19, 23.68, 53.06, 61.91, 62.84, 162.89.

Ethyl 2-Hydroperoxy-2-thio-*tert*-butylethanoate (5q-OOH). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.32 (t, $J = 7.2$ Hz, 3H), 1.45 (s, 9H), 4.28−4.30 (m, 2H), 5.53 (s, 1H), 9.41 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 13.97, 31.17, 45.62, 62.13, 84.02, 168.95.

Ethyl 2-Hydroxy-2-thio-*tert*-butylethanoate (5q-OH). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.23 (t, $J = 7.2$ Hz, 3H), 1.36 (s, 9H), 3.33 (d, $J = 10.3$ Hz, 1H), 4.14−4.21 (m, 2H), 5.27 (d, $J = 10.3$ Hz, 1H).

Ethyl 2-Oxo-thiopropionate. ^{1}H NMR ($CDCl_3$) δ 1.29 (t, $J = 7.5$ Hz, 3H), 2.41 (s, 3H), 2.93 (q, $J = 7.5$ Hz, 2H). ^{1}H NMR (C_6D_6) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.83 (s, 3H), 2.53 (q, $J = 7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.30, 23.28, 24.08, 191.49, 193.54. Anal. Calcd for $C_5H_8O_2S$: C, 45.43; H, 6.10. Found: C, 46.45; H, 5.46.

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