

# Persulfoxide: Key Intermediate in Reactions of Singlet Oxygen with Sulfides

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## ABSTRACT

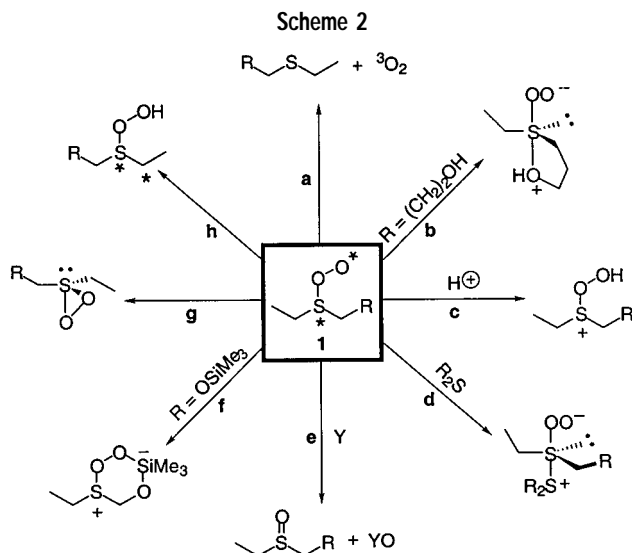
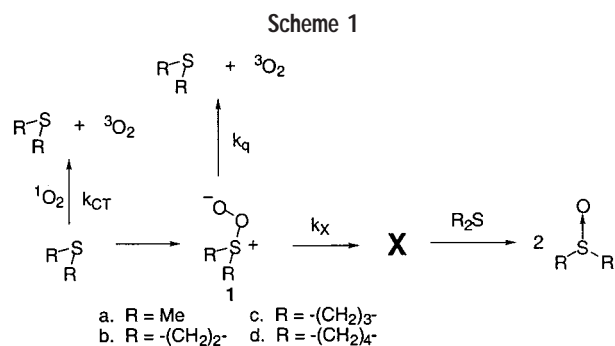
Persulfoxide ( $R_2S^+-OO^- \leftrightarrow R_2S^*-OO^*$ ) is the first formed intermediate in the reactions between singlet oxygen and organic sulfides. It is a weakly bound species that nevertheless has a sufficient lifetime to undergo a myriad of inter- and intramolecular reactions. Its behavior suggests that it can be considered as a resonance hybrid of zwitterionic and diradical canonical structures. It primarily acts as a nucleophile/base at oxygen but has a tendency to interconvert to secondary intermediates that often behave as electrophilic oxidizing agents. Judicious selection of reaction conditions and substituents can allow the use of the persulfoxide as a synthetically useful intermediate.

## Introduction

Sulfide photooxidations were first reported by Schenck and Krauch in 1962.<sup>1</sup> These oxidations are important, given the central role of sulfides in living organisms and their ability to act as antioxidants. The biochemical relevance of the sulfoxides produced in these photooxidations is also well established. Consequently, the mechanism of this important process has been subjected to intense scrutiny and is the subject of several reviews.<sup>2–5</sup>

In 1983, Foote and co-workers,<sup>6</sup> as a culmination of a seminal investigation, suggested that sulfoxide formation in the Schenck photooxidation required two intermediates on the reaction surface (**1** and **X** in Scheme 1). This requirement of two intermediates has subsequently been shown to be a general feature<sup>7</sup> in the reactions of singlet oxygen ( $^1O_2$ ) with many sulfenyl derivatives (disulfides,<sup>8,9</sup> sulfenamides,<sup>10–15</sup> and sulfonate esters<sup>11,16</sup>). In all of these photooxidations, the initially formed key intermediate has been suggested to be the persulfoxide (**1** in Scheme 1). It has the option of either decomposing via a physical quenching channel ( $k_q$  in Scheme 1) to regenerate the sulfide or reacting to form the second intermediate ( $k_x$  in Scheme 1).

Edward L. Clennan was born in 1951 in St. Paul, Minnesota. He received his B.S. degree in chemistry and mathematics from the University of Wisconsin at River Falls and his Ph.D. degree from the University of Wisconsin at Madison. Prior to joining the faculty at the University of Wyoming, he spent two years at Texas Christian University working as a postdoctoral fellow in the laboratory of Professor P. D. Bartlett. In addition, in recent years he spent a year at the National Science Foundation as a program officer and three years as Head of the Department of Chemistry at the University of Wyoming, where he is currently a Professor of Chemistry. His research interests are in the area of oxidation chemistry in homogeneous and heterogeneous media. Current projects include the study of singlet oxygen reactions in zeolites and the development of new mechanistic tools to study organic reactions in heterogeneous media.



During the past decade, we have extensively examined the photooxidations of a large number of sulfides and other divalent sulfur compounds. These studies have greatly expanded our understanding of the unique reactivity of the persulfoxide and have identified several  $k_x$  processes. In this account, we summarize our findings within the framework of the rosette presented in Scheme 2. We begin at the core of the rosette and describe the structural features of the persulfoxide itself, which play an important role in many of its reactions.

## Structure

Several attempts to make persulfoxides by nonsinglet oxygen routes for spectroscopic and/or chemical observation have been reported.<sup>17,18</sup> Akasaka and co-workers<sup>19</sup> observed formations of persulfoxides **2–4** at 13 K by irradiation into the broad sulfide–oxygen charge-transfer bands. Formations of the persulfoxides were substantiated by isotopic labeling experiments with  $^{16}O$ – $^{18}O$  which resulted in splitting of the assigned S–O stretching vibrations into two bands, thereby verifying the presence of two nonequivalent oxygen atoms. Jensen,<sup>5</sup> however, has questioned these assignments, pointing out the poor agreement with MP2/6-31G\* vibrational frequencies. He also pointed out that a thiadioxirane, **5**, a potential

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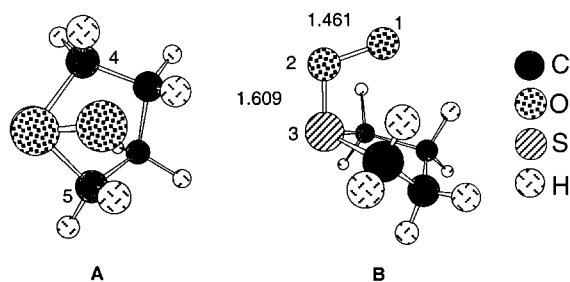
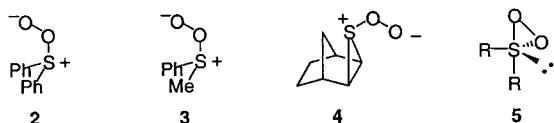


FIGURE 1.

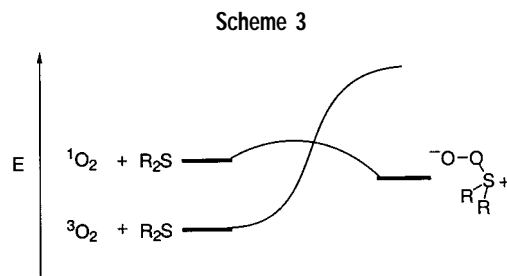
candidate for intermediate **X** in Scheme 1, has nonequivalent oxygens and its calculated vibrational frequencies are much closer to the experimentally observed values.



The inability to spectroscopically detect persulfoxides under typical photooxidative conditions has hindered progress in examining their reactivity. Persulfoxides **1a–d**, however, have been located at several theoretical levels partially obviating this unfortunate circumstance.<sup>5,20</sup> The MP2/6-31G\* geometry for **1d** is shown in Figure 1. Perhaps the most unusual feature of these persulfoxides is the placement of the outer oxygen above the carbon framework nearly bisecting (perspective A in Figure 1) the C<sub>4</sub>–S–C<sub>5</sub> angle. The S–O<sub>2</sub> bond lengths in **1a** (1.644 Å), **1b** (1.668 Å), **1c** (1.621 Å), and **1d** (1.609 Å) are all considerably longer than the 1.51 Å S–O bond length in dimethyl sulfoxide indicative of a weak S–O bond. The O–O bond lengths in **1a** (1.437 Å), **1b** (1.420 Å), **1c** (1.433 Å), and **1d** (1.461 Å), however, are very similar to the 1.47 Å O–O bond length in hydrogen peroxide. The sulfur outer oxygen distances (2.513 Å in **1a** and 2.470 Å in **1d**) are all much longer than even the typical 1.85 Å apical sulfur–oxygen bond length in sulfuranes,<sup>21</sup> indicative of the absence of a significant bonding interaction between sulfur and the outer oxygen.

### Physical Quenching (Path a in Scheme 2 or $k_q$ in Scheme 1)

Dialkyl sulfide photooxidation in aprotic solvents is an extremely inefficient process. Less than 5% of the encounters between the sulfide and singlet oxygen ( $^1\Delta_g$ ) are chemically productive. The preponderance of experimental evidence suggests that physical quenching via decomposition of the persulfoxide intermediate (Path a, Scheme 2) is responsible for the reaction inefficiency. Dialkyl sulfides do not have an appropriate low-lying excited state to deactivate (physically quench)  $^1\text{O}_2$  by an electronic energy-transfer mechanism. The lack of a correlation between the oxidation potentials ( $E_{1/2}$ ) and the rate constants for reactions of thioanisoles with  $^1\text{O}_2$  also argues against a charge-transfer physical quenching mechanism.<sup>22</sup> A much better correlation exists with the rate constants for nucleophilic reactions involving the sulfide



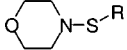
lone pairs.<sup>22</sup> In addition, kinetic analyses demonstrate that the other processes depicted in the rosette in Scheme 2 competitively inhibit physical quenching.

Physical quenching is efficient as a result of the very flat energy surface for persulfoxide formation.<sup>20</sup> Consequently, movement along the reaction surface between the persulfoxide and the singlet oxygen sulfide reaction partners is facilitated. This movement brings the persulfoxide into a region near the rapidly rising triplet oxygen–sulfide potential energy surface where intersystem crossing can effectively occur (Scheme 3). Any environmental and/or structural feature that stabilizes the persulfoxide, or removes it rapidly from solution, will therefore inhibit physical quenching. Physical quenching is often detected by comparing the rate constant of substrate induced singlet oxygen removal,  $k_T$ , to the rate constant for product formation  $k_r$  using the equation  $k_T = ak_r + k_Q$ . The variable  $a$  in this equation is a function of the product composition. When the sulfoxide is the exclusive product,  $a = 0.5$ , because for each molecule of singlet oxygen that disappears two molecules of product are formed.

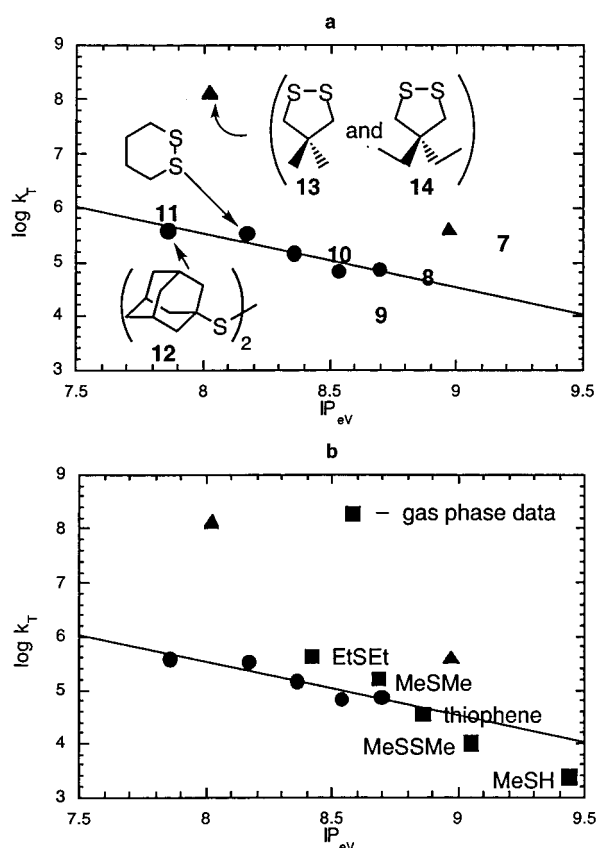
Exchange of an alkyl group in the persulfoxide with an amine to give a persulfonamide is a structural change which has a dramatic effect on the contribution of the physical quenching channel (Path a in Scheme 2).<sup>10,12</sup> The persulfonamide formed in the reaction of 4-morpholinyl benzyl sulfide, **6a**, does not exhibit any propensity to decompose via a physical quenching channel, and decompositions of the persulfonamides formed in photooxidations of alkyl (**6b–e**) and aryl (**6f–i**) sulfenamides (Table 1) are dramatically suppressed (for comparison, % physical quenching  $\text{Et}_2\text{S} > 95\%$ ). Steric effects appear to have little effect in directing the decomposition of the persulfonamide along the physical quenching channel (Table 1). On the other hand, intensification of the positive charge on the persulfonamide sulfur in the aryl sulfenamides, **6f–i**, increases the contribution of the physical quenching channel from 73 to 87%.

When persulfoxide formation is suppressed, other mechanisms for physical deactivation of singlet oxygen are allowed to contribute. This situation is encountered during photooxidations of disulfides.<sup>8,9</sup> A plot of  $\log(k_T)$  versus  $\text{IP}_{\text{eV}}$  for disulfides shown in Figure 2a is linear with the exceptions of dimethyldisulfide, **7**, and 4,4-dimethyl-, **13**, and 4,4-diethyl-1,2-dithiolane, **14**, which deviate significantly from the linear regression line. The linear relationship is indicative of a charge-transfer mechanism ( $k_{\text{CT}}$  in Scheme 1) in which the charge transfer states are mixed with the ground states of the complex. Consistent

**Table 1. Kinetic Data for the Photooxidations of Sulfenamides 6a–i<sup>a</sup>**

	$k_T$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>	$k_r$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup>	$k_Q$ (M <sup>-1</sup> s <sup>-1</sup> ) <sup>d</sup>	%Physical Quenching
<b>6a</b> R = PhCH <sub>2</sub> -	1.28 × 10 <sup>6</sup>	2.94 × 10 <sup>6</sup>	0	0
<b>6b</b> R = Me-	1.46 ± 0.12 × 10 <sup>7</sup>	7.59 ± 0.04 × 10 <sup>6</sup>	1.06 × 10 <sup>7</sup>	74 ± 2
<b>6c</b> R = Et-	8.85 ± 0.57 × 10 <sup>6</sup>	4.63 ± 0.16 × 10 <sup>6</sup>	6.44 × 10 <sup>6</sup>	74 ± 2
<b>6d</b> R = iPr-	3.51 ± 0.02 × 10 <sup>6</sup>	2.06 ± 0.07 × 10 <sup>6</sup>	2.36 × 10 <sup>6</sup>	70 ± 2
<b>6e</b> R = tBu-	7.13 ± 0.78 × 10 <sup>4</sup>	4.34 ± 0.69 × 10 <sup>4</sup>	4.87 × 10 <sup>4</sup>	69 ± 2
<b>6f</b> R = pMeC <sub>6</sub> H <sub>4</sub> -	2.61 × 10 <sup>5</sup>	1.40 ± 0.15 × 10 <sup>5</sup>	1.88 × 10 <sup>5</sup>	73 ± 2
<b>6g</b> R = C <sub>6</sub> H <sub>5</sub> -	2.32 × 10 <sup>5</sup>	8.04 ± 0.39 × 10 <sup>4</sup>	1.89 × 10 <sup>5</sup>	82 ± 2
<b>6h</b> R = pClC <sub>6</sub> H <sub>4</sub> -	1.13 × 10 <sup>5</sup>	3.61 ± 0.49 × 10 <sup>4</sup>	9.35 × 10 <sup>4</sup>	84 ± 2
<b>6i</b> R = pNO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	2.39 × 10 <sup>4</sup>	5.82 ± 0.78 × 10 <sup>3</sup>	2.01 × 10 <sup>4</sup>	87 ± 2

<sup>a</sup> In benzene. <sup>b</sup> The rate constant for substrate induced removal of singlet oxygen determined by quenching time-resolved emission of singlet oxygen at 1270 nm. <sup>c</sup> Rate constant for chemical reaction. <sup>d</sup> Rate constant for physical quenching.



**FIGURE 2.** a.  $\log(k_T)$  versus photoelectron spectroscopy ionization potentials of MeSSMe, **7**; EtSSEt, **8**; PrSSiPr, **9**; tBuSStBu, **10**; 1,2-dithiacyclohexane, **11**; 2-adamantylidysulfide, **12**; 4,4-dimethyl-1,2-dithiolane, **13**; and 4,4-diethyl-1,2-dithiolane, **14**. b.  $\log(k_T)$  versus  $IP_{eV}$  for several substrates in the gas phase superimposed on the data from Figure 2a.

with this analysis is the fact that gas-phase  $k_T$  values for methanethiol, **7**, dialkylsulfides, and thiophene also fall

remarkably close to the correlation line (Figure 2b). Charge-transfer quenching is likely to be the dominant mechanism for quenching by these substrates, because the buildup of charge necessary to form a persulfoxide is unlikely to be tolerated in the gas phase.

The deviations of dimethyldisulfide and the two 1,2-dithiolanes from the linear regression line reflect their ability to form the corresponding persulfoxides. The small steric demands of the methyl groups in **7** and the constrained  $\angle\text{CSSC}$  dihedral angle of only 30° in **13** and **14** allow access to the disulfide linkage to form the persulfoxide. Consequently, two mechanisms contribute to the quenching of singlet oxygen by these substrates. The persulfoxide mechanism is clearly the more efficient mechanism when persulfoxide formation is sterically allowed and the substrate has an appropriate HOMO energy.

### Hydroperoxy Sulfurane Formation (Path b in Scheme 2)

Foote and Peters reported that physical quenching of <sup>1</sup>O<sub>2</sub> by diethylsulfide and 1,4-dithiane was suppressed in methanol and in wet acetonitrile.<sup>23</sup> This observation led to the speculation that the persulfoxide might be stabilized in protic media by addition to form a sulfurane<sup>24</sup> (Path b, Scheme 2). The formation of hydroperoxy sulfurane **15** has been suggested during the reaction of an alkoxy-sulfurane with hydrogen peroxide (Scheme 4).<sup>17,25</sup> However, the hydroperoxy sulfuranes in this reaction and in <sup>1</sup>O<sub>2</sub> reactions have escaped direct spectroscopic characterization.

Kinetic evidence implicating a hydroperoxy sulfurane was obtained by examination of a series of sulfides, **16**, (Figure 3) in which a hydroxy group was attached via a variable length tether. The chemical rate constants,  $k_r$ , are

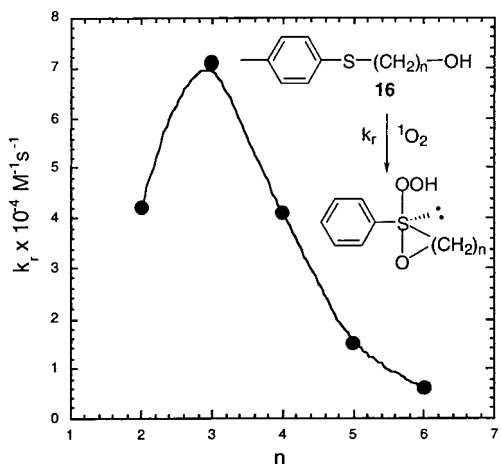
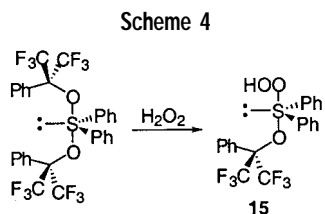


FIGURE 3.



very sensitive to the number of intervening methylenes with the maximum value observed when  $n$  is equal to 3 (Figure 3).<sup>26,27</sup> When  $n = 6$ , the hydroperoxy sulfurane contains an eight-membered ring rather than the thermodynamically favorable five-membered ring, and as a result,  $k_r$  is more than an order of magnitude smaller than when  $n = 3$ .

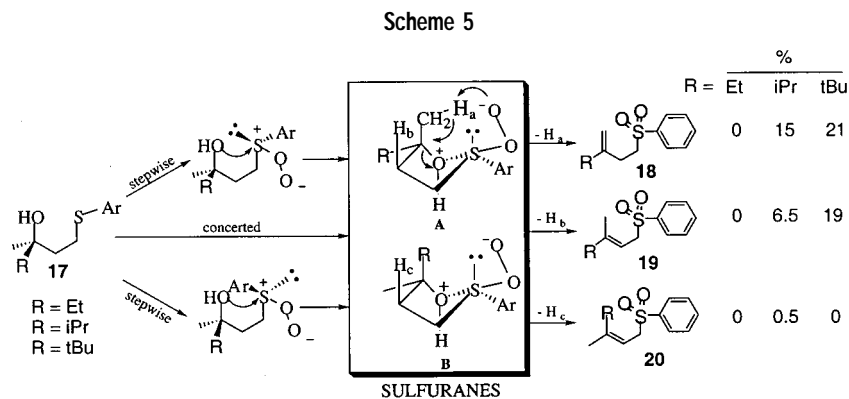
Perhaps the most compelling evidence for the formation of a sulfurane came from the study of a series of *gem*-dialkyl-substituted  $\gamma$ -hydroxy sulfides, **17**. Photooxidations of these compounds resulted in formation of several alkenes, **18**, **19**, and **20**, in addition to the anticipated sulfoxides and sulfones. The formation of the alkenes can be rationalized by intramolecular hydrogen abstraction in the two diastereomeric sulfuranes which form by addition of the hydroxy group to the sulfonium sulfur in the persulfoxide as depicted in Scheme 5. Photolysis of a sample of **17** ( $R = tPr$ ) in which the hydroxy group was specifically labeled with  $^{17}O$  resulted in quantitative transfer of the label to the sulfonyl sulfur consistent with this mechanism.

These results unambiguously demonstrate sulfurane formation during photooxidations of these  $\gamma$ -hydroxy sulfides. However, kinetic data<sup>26</sup> also demonstrate that its efficiency is so low [ $k_r/k_T = (7.1 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1} / (2.29 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1} = 0.03$  for **16** ( $n = 3$ )] that it is unlikely to be responsible for the total inhibition of physical quenching observed during the photooxidations of sulfides in methanol. A more likely candidate for competitive inhibition in protic solvents is protonation of the persulfoxide (path c, Scheme 2).

### Hydroperoxy Sulfonium Ion Formation (Path c in Scheme 2)

Protonation of the pendant oxygen in the persulfoxide (Path c in Scheme 2) is expected to be a very facile process for several reasons: (1) the persulfoxide has distinct zwitterionic character as supported by Mulliken HF/6-31G\* analyses which reveal substantial charge on sulfur (+0.95 on **1a**,<sup>5</sup> +0.80 on **1b**,<sup>28</sup> 0.95 on **1c**,<sup>28</sup> 0.99 on **1d**<sup>28</sup>) and a negative charge which is nearly equally distributed on both the inner and outer oxygen atoms and (2) proton transfers between heteroatoms are very rapid.<sup>29</sup> Analyses of the effects of the additions of various alcohols to benzene solutions of diethylsulfide support this conclusion.<sup>30</sup> The chemical rate constant,  $k_r$ , for diethylsulfide formation increases by more than an order of magnitude with the addition of only 1.5% methanol to a benzene solution of diethylsulfide. In addition, the number of encounters between diethylsulfide and  $^1O_2$  which lead to physical quenching decreases from 94% to only 16% as the methanol concentration is increased from 0 to 1.84 M.<sup>30</sup> Indeed, the intercept-to-slope ratio of a plot of  $1/k_r$  versus  $1/[MeOH]$  for these experiments (Figure 4a) reveals that protonation of the persulfoxide,  $k_x$ , is approximately 2.4 times as rapid as physical quenching,  $k_q$  (Path a in Scheme 2). In addition, a plot of  $\log(k_x[ROH]/k_x[MeOH])$  versus  $pK_a$  of a series of alcohols is linear (Figure 4b).

The lack of a correlation between the efficacy of physical quenching inhibition by a series of alcohols and the Taft steric parameter<sup>30</sup> suggests that sulfurane formation, in which steric effects should be important, plays little or no role. Nevertheless, we suggested that methanol, because of its small size, might simultaneously hydrogen bond and add to the sulfonium sulfur in a concerted



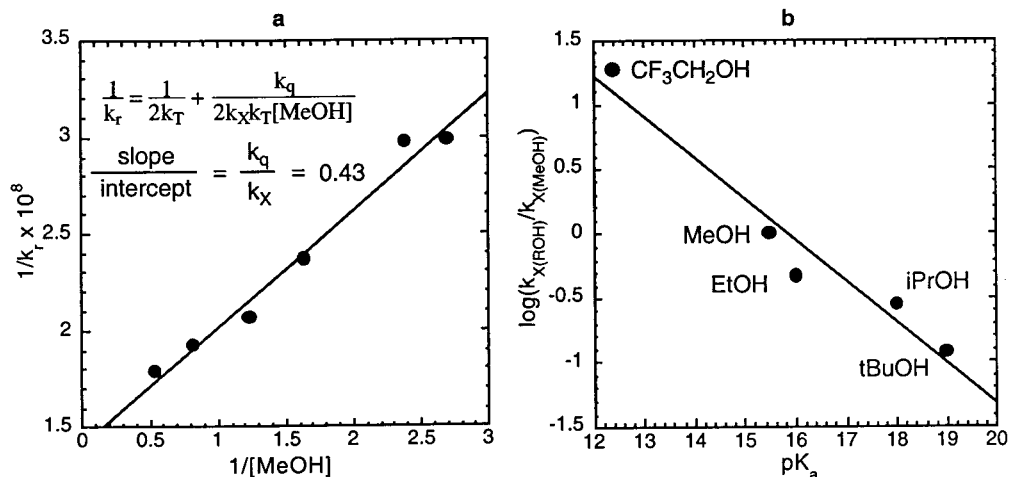
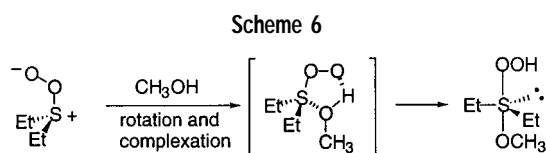


FIGURE 4.



addition pathway (Scheme 6). On the other hand, protonation by the very non-nucleophilic but reasonably acidic 2,2,2-trifluoroethanol ( $pK_a = 12.4$ ) undoubtedly contributes far more than addition to sulfur in its ability to inhibit physical quenching. Recently, Bonesi and Albini<sup>31</sup> came to a similar conclusion but went a step further to suggest that even in the case of methanol there is no nucleophilic component to its ability to suppress physical quenching.

### Sulfide Addition (Path d in Scheme 2)

Sulfide addition to the persulfide does not occur consistent with the paradigm that suggests that nucleophilic attack at the sulfonium ion-like sulfur is prohibitively difficult. An exception to this generalization, however, is observed during the photooxidation of thietane, **21**.<sup>32</sup> Diethylsulfide and **21** both quench the emission of singlet oxygen at 1270 nm with similar efficiency ( $k_T[\text{Et}_2\text{S}] = (3.04 \pm 0.52) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_T[\mathbf{21}] = (3.13 \pm 0.22) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ). However, the amount of product formed at a given time of irradiation, under conditions where all the singlet oxygen is captured, is independent of substrate concentration during  $\text{Et}_2\text{S}$  photooxidation but dependent on substrate concentration during photooxidation of **21** (Figure 5a).

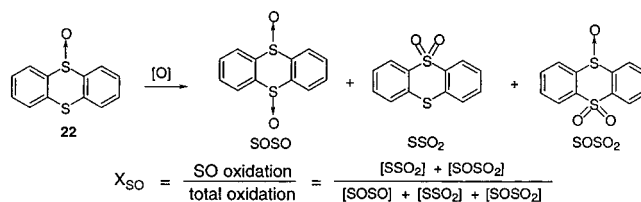
The unusual increase of product formation with increasing concentration of **21** is due to competitive inhibition of physical quenching by nucleophilic addition of **21** to thietane persulfide to give a sulfurane-like intermediate (Scheme 7). The linear correlation observed when  $1/k_r$  is plotted versus  $1/[\mathbf{21}]$  (Figure 5b) is consistent with this mechanism. The intercept/slope ratio in Figure 5b ( $k_X/k_q$ ) reveals that sulfide addition is approximately six times faster than decomposition of the persulfide (Path a in Scheme 2). The unique behavior of **21** is a result of a small C–S–C angle of  $78^\circ$  that allows an unencumbered approach to the sulfur in the persulfide. This approach is

sterically prohibited in other sulfides with larger C–S–C angles (e.g.,  $98.9^\circ$  in  $\text{Et}_2\text{S}$ ).

### Oxygen Atom Transfer (Path e in Scheme 2)

The ability of persulfides to transfer an oxygen atom to substrates Y (Path e Scheme 2) has attracted attention because of the interest in monooxygenase enzyme models.<sup>33</sup> The spectrum of Y substrates which have been examined includes electrophilic substrates such as sulfoxides,<sup>6,34</sup> sulfinate esters,<sup>35</sup> sulfenamides,<sup>35</sup> phosphites,<sup>36</sup> and sulfenate esters.<sup>16</sup> Nucleophilic substrates such as alkyl substituted alkenes, on the other hand, do not function as oxygen atom acceptors.

The transfer of an oxygen atom to diphenyl sulfoxide ( $\text{Ph}_2\text{SO}$ ) has been used to explore the mechanism of diethyl sulfide photooxidation.<sup>6,34</sup> These studies took advantage of the fact that  $\text{Ph}_2\text{SO}$  is unreactive toward  $^1\text{O}_2$  but efficiently reacts with diethyl persulfide to give diethylsulfoxide and diphenylsulfone. Sawaki and Ogata<sup>37</sup> reported that dimethylpersulfide behaves as a nucleophilic oxygen transfer agent (Hammett  $\rho = +0.25$ ) in its reactions in benzene with a series of aryl substituted sulfoxides. The nucleophilicity of dimethyl persulfide, however, was significantly reduced in methanol and exhibited a Hammett  $\rho$  value of  $-0.05$ . The authors attributed the reduced nucleophilicity to hydrogen bonding with methanol. The ability of sulfoxides to trap nucleophilic peroxidic species has subsequently been utilized in the design and use of thianthrene 5-oxide, **22**, as a mechanistic probe in many oxygen transfer reactions.<sup>38–42</sup> The probe allows placement of an oxidant on the  $X_{\text{SO}}$  scale by measuring the ratio of product from oxidation at the sulfinyl (SO) sulfur to product from oxidation at the sulfenyl (S) sulfur.<sup>43</sup>



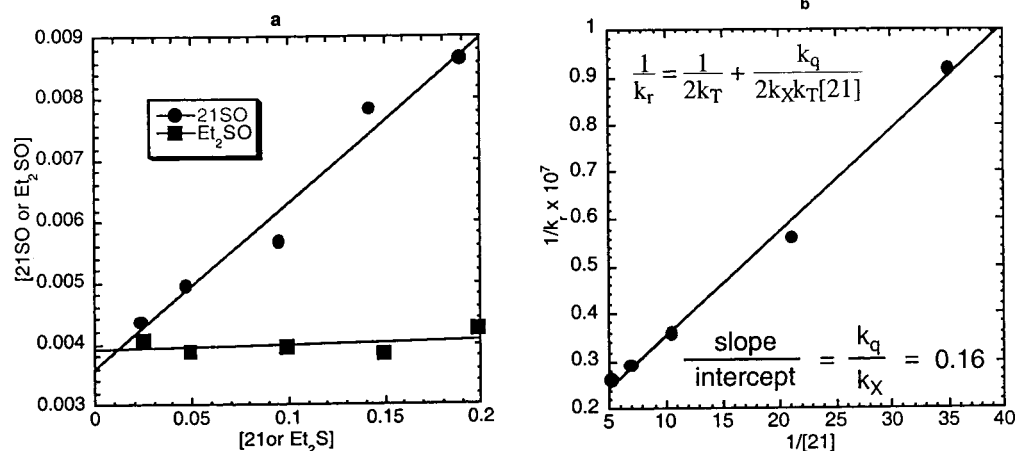
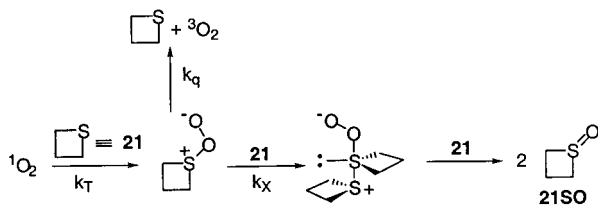


FIGURE 5.

Scheme 7



The relative rate constants for oxygen transfer from diethyl persulfoxide to several substrates are given in Table 2. The sulfinamide is the least reactive as a result of resonance delocalization of the nitrogen lone pair that reduces the electrophilicity at sulfur. Two different mechanisms could be envisioned for oxygen transfer to (PhO)<sub>3</sub>P, to other phosphites, and to sulfenates (e.g., PhS-OEt): a bifilic process (A in Scheme 8) or a nucleophilic addition to form an anionic hypervalent intermediate (B in Scheme 8). The bifilic process that involves a concerted insertion of the sulfur or phosphorus into the O–O bond has been established for the reactions of Ph<sub>3</sub>P with several strained peroxides; however, it is unlikely to operate during the reactions of the substantially less nucleophilic sulfenates or phosphites. Instead, nucleophilic additions to both phosphites<sup>44</sup> and sulfenates<sup>45</sup> to form hypervalent intermediates have ample precedent and are the likely mechanistic scenarios for these reactions.

### Silicate Anion Formation (Path f in Scheme 2)

Photooxidations of  $\alpha$ -trimethylsiloxysulfide, **23**, at low concentrations generated silicate **24** as the major product (Scheme 9).<sup>46</sup> Conspicuously absent from the reaction mixtures were the anticipated sulfoxide, **25**, and the corresponding sulfone. The novel structure of **24** was convincingly established by a combination of <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT, and C,H-COSY experiments.

The mechanism of formation of **24** occurs by nucleophilic attack of the persulfoxide on the appended trimethylsiloxy group to give trimethylsilicate intermediate **26** which subsequently rearranges to **24** by a methyl migration from silicon to oxygen. The rearrangement of **26** to

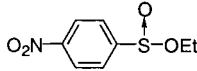
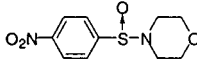
**24** has ample precedent in migrations from silicon to carbon. The intermediacy of **26** is supported by the fact that incrementally increasing the concentration of **23** from 0.002 to 0.3 M resulted in the appearance and formation of increasing amounts of sulfoxide **25**. Control reactions also demonstrated that the reaction of **23** with **24** is not the source of sulfoxide formation. In addition, increasing concentrations of **23** do not competitively inhibit physical quenching, providing corroboration for the persulfoxide intermediate. The persulfoxide formed from **23** is 10 times more difficult to trap by oxygen transfer to Ph<sub>2</sub>SO than diethylpersulfoxide. Furthermore, physical quenching accounts for 95% of the interactions of <sup>1</sup>O<sub>2</sub> with diethylpersulfoxide but only 45% of the interactions with **23**. Both of these observations point to a reduced lifetime of the persulfoxide and the efficiency of its addition to the trimethylsiloxy group to form **26**.

### Thiadioxirane Formation (Path g in Scheme 2)

Thiadioxiranes have attracted considerable interest because of their topographical similarity to the synthetically useful dioxiranes. A large number of different thiadioxiranes, **27** and **28**, have been located by ab initio calculations at the MP2/6-31G\* level (Scheme 10).<sup>5,14,28</sup> The geometries are best described as distorted trigonal bipyramidal, with ligands that reside in either equatorial or apical positions. The apical S–O bonds are longer than the equatorial S–O bonds, and natural bond order analyses reveal more negative charge at the apical than equatorial oxygen.

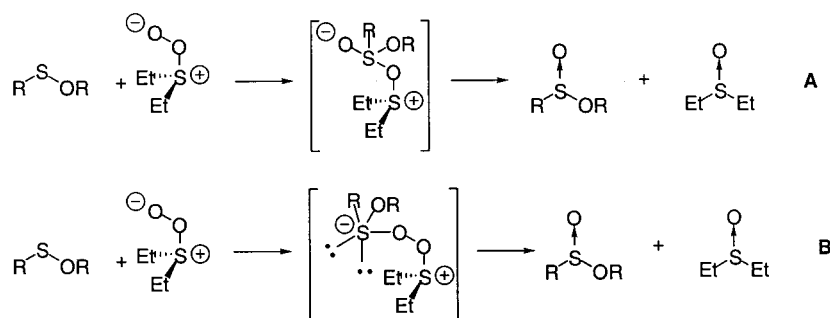
Transition states for interconversion of all the persulfoxides to the thiadioxiranes have been located with the exception of **28** (*n* = 2). The activation barriers decrease from 27.3 to 10.2 kcal/mol in the substituent (X) order Cl > CH<sub>3</sub> ≈ NH<sub>2</sub> > OCH<sub>3</sub> ≈ SCH<sub>3</sub> > F. The activation barriers for the formation of the spirothiadioxiranes **28** (*n* = 0, 2) and for dimethylthiadioxirane, **27a**, are remarkably similar at approximately 20 kcal/mol. These barriers are extremely high and make it unlikely that formation of a thiadioxirane can compete with the other processes shown in Scheme 2. Consequently, a thiadioxirane is an unlikely candidate

Table 2. Relative Rate Constants for Oxygen Transfer Reactions of Diethylpersulfoxide

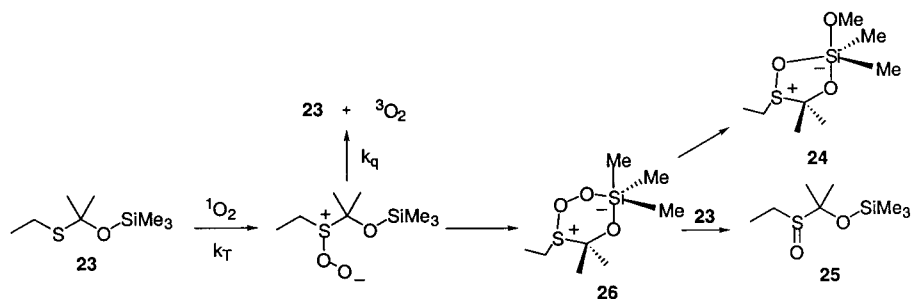
	$k_{\text{relative}}$		$k_{\text{relative}}$
	2.35 <sup>a</sup>	$(\text{PhO})_3\text{P}$	20.9 <sup>a</sup> 28 <sup>b</sup>
$\text{Ph}_2\text{SO}$	1.0 <sup>a</sup>		0.18 <sup>a</sup>

<sup>a</sup> In benzene. Clennan, E. L.; Stensaas, K. L.; Rupert, S. D. *Heteroat. Chem.* **1998**, *9*, 51–56. <sup>b</sup> In  $\text{CH}_3\text{CN}$ . Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909–1910.

Scheme 8



Scheme 9



for the second intermediate, **X**, (Scheme 1) on the Foote reaction surface. A more viable candidate is the hydroperoxy sulfonium ylide discussed in the following section.

### Hydroperoxy Sulfonium Ylide Formation (Path h in Scheme 2)

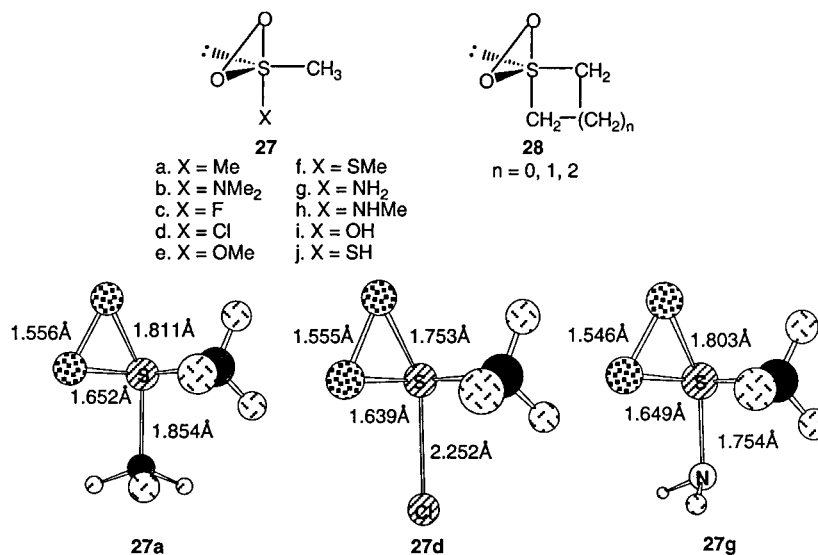
Intramolecular abstraction of a proton or a hydrogen atom from the  $\alpha$ -carbon in the persulfide by the terminal oxygen atom generates, respectively, a zwitterionic ( $\cdot/\cdot = +/\cdot$  in Scheme 2) and diradical ( $\cdot/\cdot = \cdot/\cdot$  in Scheme 2) *S*-hydroperoxysulfonium ylide, **29**.<sup>47,48</sup> The two ylides are isomers rather than resonance structures and can be visualized as having distinctly different placements of the peroxy hydrogen (vide infra). The formation of both isomers is consistent with, but is not demanded by, extensive studies with sulfides bearing radical and/or anion stabilizing substituents.<sup>49,50</sup> The dichotomous formations of two *S*-hydroperoxysulfonium ylides reflect the contributions of both diradical and zwitterionic resonance forms to the electronic character of the persulfide

precursor. Schenck originally depicted the persulfide as a diradical;<sup>51</sup> however, its idiosyncratic behavior which also justified its depiction as a zwitterion was subsequently recognized by Foote and co-workers.<sup>23</sup>

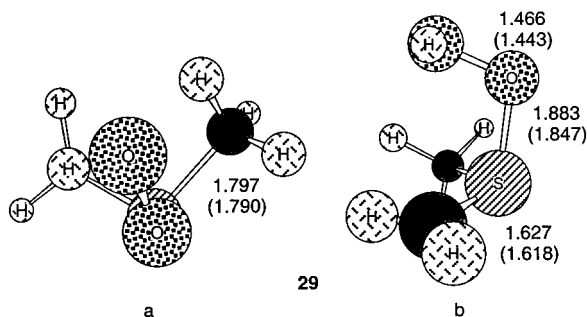
The zwitterionic dimethyl hydroperoxysulfonium ylide, **29**, was established as a viable species on the MP2/6-31G(d) and MP2/6-311+G(2df) ab initio surfaces.<sup>20</sup> It has a short S–CH<sub>2</sub> bond indicative of double bond character and an O–O bond that bisects the C–S–C angle (Scheme 11). The most stable conformation has the peroxy hydrogen directly over the CH<sub>2</sub> at a distance of 3.15 Å. Three other conformations which were located do not have the peroxy hydrogen above the CH<sub>2</sub> group and are 1.5, 2.1, and 2.2 kcal/mol higher in energy, implying the existence of a very nonlinear hydrogen bond in **29** worth approximately 1–1.5 kcal/mol.

G2-extrapolated CCSD(T)/6-311+G(2df) energies reveal that conversion of the persulfide to **29** is exothermic by 6 kcal/mol.<sup>20</sup> In addition, a transition structure connecting the persulfide and **29**, which was confirmed by

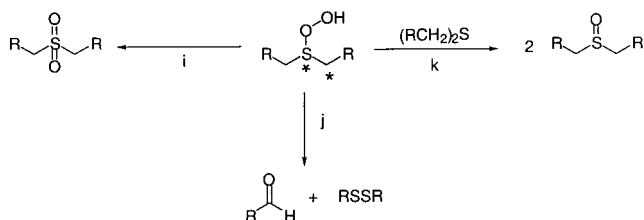
Scheme 10



Scheme 11. a. Hydroperoxysulfonium Ylide **29** 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<sub>3</sub> Bond Length and b. Hydroperoxysulfonium Ylide **29** Looking down the H–O Bond Showing the Planar CH<sub>2</sub> and the O–O, S–O, and S–CH<sub>2</sub> Bond Lengths



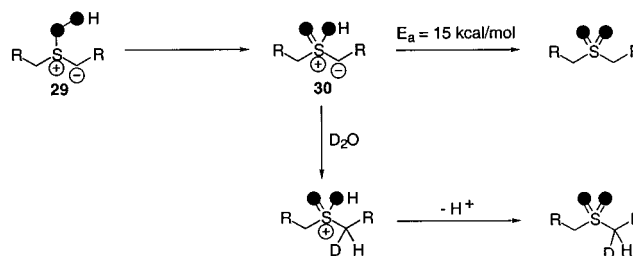
Scheme 12



frequency calculations and by tracing the intrinsic reaction coordinate (ICR), is 6 kcal/mol higher in energy than the persulfoxide. Consequently, the reversion of **29** to the persulfoxide is 12 kcal/mol uphill and does not compete with interconversion of the *S*-hydroperoxysulfonium ylide to product. In fact, the ylide has been experimentally implicated in formation of several different products as shown in Scheme 12.

The mechanism of unimolecular sulfone formation (Path i in Scheme 12) involves a very exothermic (>40 kcal/mol) migration of OH from the peroxy linkage to sulfur to form a protonated sulfone ylide, **30** (Scheme 13).<sup>20</sup> The migration is then followed by an intramolecular keto–enol tautomerism with a significant barrier of 15

Scheme 13



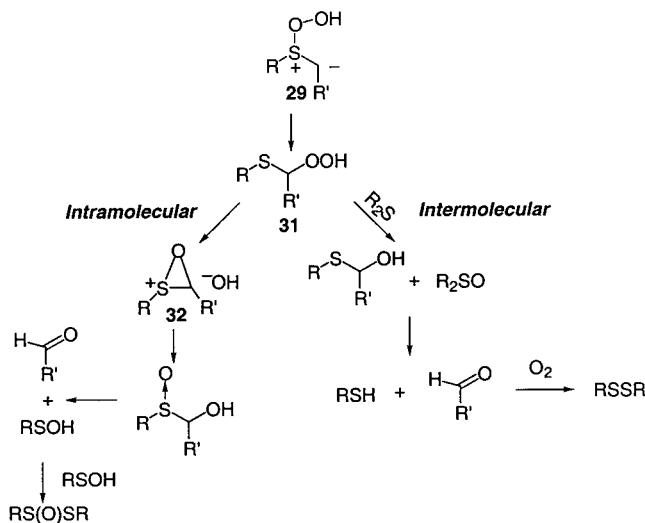
kcal/mol to give the sulfone product. This mechanistic picture (Scheme 13) is supported by computational evidence<sup>20</sup> and by experimental evidence that demonstrates that both oxygen atoms in the sulfone product had their origin in the same oxygen molecule. In addition, the ability to incorporate a single deuterium atom at the  $\alpha$ -carbon atom with added D<sub>2</sub>O is consistent with a high barrier for the keto–enol tautomerism.<sup>52</sup> In contrast, sulfone formed intermolecularly via trapping with adventitious sulfoxide (Path e, Scheme 1) contains oxygen atoms from different oxygen molecules and does not incorporate deuterium.

The oxidative cleavage reaction (Path j in Scheme 12) occurs via an  $\alpha$ -hydroperoxysulfide, **31**, (Scheme 14) which forms from the hydroperoxysulfonium ylide by a Pummerer rearrangement. The  $\alpha$ -hydroperoxysulfide can be isolated in excellent yield (>95%) at lower temperatures (<0 °C) when the sulfide contains an electron withdrawing group<sup>49,50</sup> (e.g., PhSCH<sub>2</sub>CO<sub>2</sub>Et). The lifetime of the  $\alpha$ -hydroperoxysulfide appears to be limited by the mechanism of its cleavage. In most sulfides, a rapid intramolecular pathway occurs to generate the carbonyl compound and a mechanistically significant thiolsulfinate. In sulfides with electron withdrawing groups, the oxathiiranium ion, **32**, is destabilized, and an intermolecular pathway predominates to form a disulfide rather than a thiolsulfinate cleavage product.

Path k in Scheme 12 represents the second step on the Foote reaction surface for sulfide photooxidation (Scheme 1). In much of the earlier literature, we and others<sup>4</sup> had

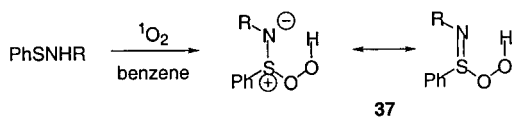


Scheme 14



assumed that the second intermediate **X** was the thia-dioxirane. However, the 6 kcal/mol barrier for the formation of **29** (vide supra) is more compatible with the experimental requirement for rapid interconversion of the persulfoxide to **X** than is the 20 kcal/mol barrier necessary to form the thia-dioxirane. Several experimental studies have provided compelling evidence for this conclusion. For example, photooxidations of 1,3-dithianes, **33** and **34**, and their 2-deuterated analogues, which react exclusively to give a single sulfoxide product, give substantial isotope effects.<sup>53</sup> In addition, the formation of ethylvinylsulfide during photooxidation of **35** can most reasonably be rationalized by invoking a  $\beta$ -elimination in a *S*-hydroperoxysulfonium ion intermediate.<sup>54</sup> Although it now appears that **29** is **X** in the vast majority of sulfide photooxidations, there are some sulfides (e.g., **36**)<sup>55</sup> which do react, albeit slowly, to produce sulfoxide by a yet undetermined mechanistic route.

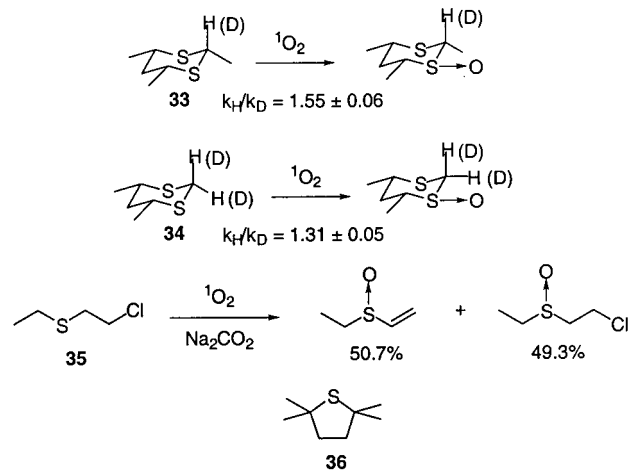
Photooxidations of *N*-substituted sulfenamides generate iminopersulfenic acids, **37**, which are isoelectronic to *S*-hydroperoxysulfonium ylides.<sup>14,15</sup> They exhibit the ability to epoxidize norbornene; a feature which is reminiscent of the behavior of some *S*-hydroperoxysulfonium ylides<sup>56</sup> and justifies their characterization as persulfenic acids.



## Summary

The persulfoxide is a weakly bound intermediate on the singlet oxygen sulfide reaction surface. Nevertheless, it plays an important role in the chemical modifications of organic sulfides and methionine containing biopolymers.<sup>57</sup> Intra- and intermolecular reactions at both the terminal oxygen atom and at sulfur can compete effectively with dissociation to sulfide and triplet oxygen under a variety of conditions. Computationally, it is clear that the thia-dioxirane, **5**, is on the sulfide singlet oxygen reaction surface. However, it is equally clear that it is kinetically

Scheme 15



inaccessible in these reactions. Consequently, the thia-dioxirane, **5**, remains an intriguing, but as yet elusive, isomer of the fascinating persulfoxide that represents an important synthetic target.

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