Photooxidation of Sulfenic Acid Derivatives. 4.[1,2] Reactions of Singlet Oxygen with Sulfenamides

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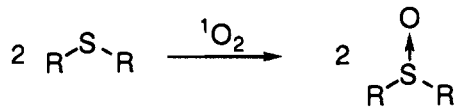
Abstract: The reactions of singlet oxygen with nine sulfenamides are reported. A detailed kinetic study reveals that two intermediates are required on the photooxidation reaction surface. One intermediate acts as a nucleophile and the second intermediate as an electrophile in their reactions with diaryl sulfoxides and diaryl sulfides, respectively. Physical quenching is also suppressed in the sulfenamides relative to other sulfur-containing singlet oxygen substrates. The mechanism of the reaction is discussed and compared to diethyl sulfide photooxidation, and a rationale for the decreased importance of physical quenching in these substrates is presented.

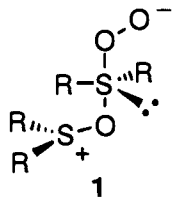
Oae and Doi[3] in their recent book on organosulfur chemistry point out that oxidation ranks with substitution and reduction as one of the three major reactions which take place at the sulfur atom. In addition, sulfide oxidation takes on added importance with the proliferation of organic synthetic procedures which utilize the sulfoxide group as a chiral auxiliary.[4] In 1962, Schenck and Krausch[5] reported a new procedure for the oxidative formation of sulfoxides which involved singlet oxygen (eq 1). Remarkably, after 32 years, a consensus opinion on the mechanism of this topographically simple reaction does not exist.



(1)

The mechanistic framework upon which much of the debate in the past 11 years has centered was suggested in 1983 by Foote and co-workers in order to rationalize the photooxidation of diethyl sulfide in benzene[6] (Scheme 1; R = X = Et). The unique feature of this mechanism is the formation of two discrete intermediates, the persulfinate, **A**, and thiadioxirane, **B**. The diethyl persulfinate (persulfoxide) partitions between decomposition (physical quenching, >95%) and interconversion to **B** (<5%), while the diethyl thiadioxirane **B** partitions between reaction with a molecule of substrate to give two sulfoxides (R_2SO) and unimolecular decomposition to form a sulfone (R_2SO_2). The experimental results which support the mechanism depicted in Scheme 1 include the following (1) Diphenyl sulfoxide (Ph_2SO) and diphenyl sulfide (Ph_2S), which are both inert to singlet oxygen are never-the-less converted to diphenyl sulfone (Ph_2SO_2) and Ph_2SO, respectively, upon co-photooxidation with diethyl sulfide (Et_2S). (2) The addition of diphenyl sulfoxide does not compete with Et_2S for an intermediate but does competitively inhibit physical quenching. (3) On the other hand, Ph_2S does not competitively inhibit physical quenching but does compete with Et_2S for an intermediate. (4) The extent of physical quenching is independent of the concentration of Et_2S. (5) Co-photooxidations of Et_2S with substituted diaryl sulfides and sulfoxides provides evidence that the first intermediate is a nucleophilic and the second intermediate an electrophilic oxidant.

In 1991, Sawaki and co-workers[7] reported that (1) sulfoxide formation is enhanced while sulfone formation is unaffected by protic or coordinating solvents, (2) sulfoxide formation is more sensitive to the electronic character but less sensitive to the steric effects of substituents than sulfone formation, (3) the sulfone/sulfoxide ratio decreases as a function of irradiation time, and (4) both oxygen atoms in the sulfone originated in the same oxygen molecule. These workers used this data to suggest that the thiadioxirane is formed in competition with persulfoxide **A** and not subsequent to its formation. They also provided speculation that intermediate **B** might be best represented as a persulfoxide coordinated to a sulfoxide, **1**.



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Theoretical treatments of sulfide photooxidations have done little to resolve the conflict between these two mechanistic proposals. In an early theoretical study of the reaction of singlet oxygen with dimethyl sulfide only the persulfoxide was located as a bound intermediate on the potential energy surface.[8] In 1991, Sawaki and co-workers[7] reported the successful location of a stable thiadioxirane on the HF/3-21G* potential energy surface. This result has subsequently been refuted by Jensen,[9] who suggests that the Sawaki thiadioxirane is an artifact from the use of a small unbalanced basis set. However, in this same report, Jensen demonstrated that the persulfoxide and thiadioxirane could both be located at the MP2/6-31G* level. In the

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(1) Part 3: Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952−7954. Part 1: Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809−810.

(2) Clennan, E. L.; Wang, D.; Zhang, H.; Clifton, C. H. *Tetrahedron Lett.* **1994**, *35*, 4723−4726.

(3) Oae, S.; Doi, J. T. *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press: Boca Raton, FL, 1991.

(4) Diter, P.; Taudien, S.; Samuel, O.; Kagan, H. B. *J. Org. Chem.* **1994**, *59*, 370−373.

(5) Schenck, G. O.; Krausch, C. H. *Angew. Chem.* **1962**, *74*, 510.

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

(7) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677−2682.

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

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

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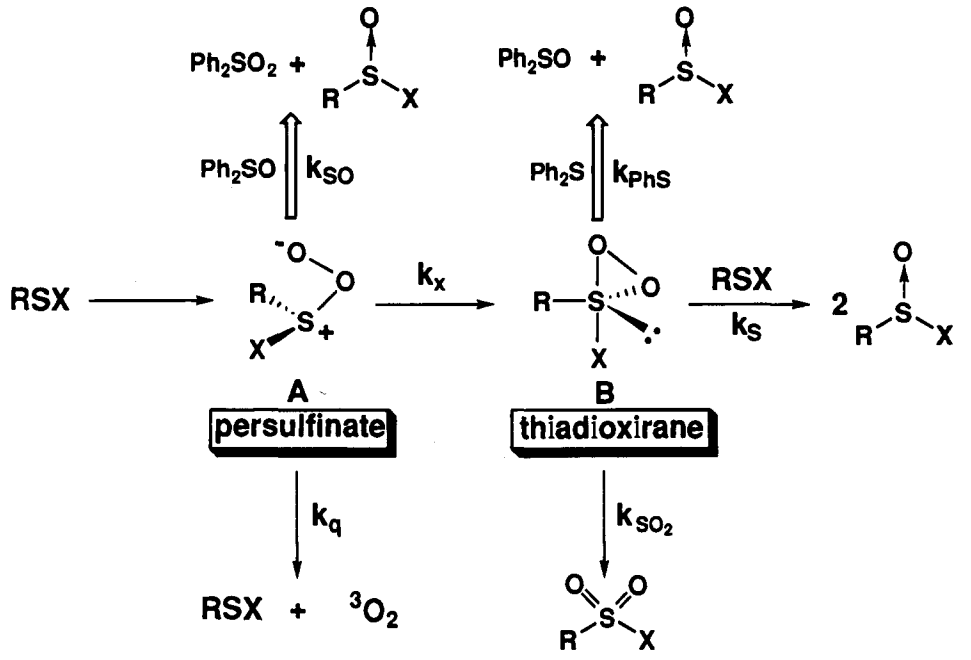
Scheme 1



X = C, SR, NR_2, OR

gas phase it appears that these two intermediates are nearly isoenergetic and are separated by an experimentally insurmountable barrier of close to 20 kcal/mol.

In order to experimentally address the problem of the identity of the second intermediate, we have initiated a program to examine the photooxidations of sulfenic acid derivatives (Scheme 1). We anticipated that as X became more electron withdrawing it would destabilize the persulfinate intermediate by intensifying the positive charge on sulfur and stabilize the thiadioxirane by increasing the electronegativity of the apical substituent in a pseudo trigonal bipyramidal environment.[10] By structurally stabilizing the thiadioxirane relative to the persulfinate, we hoped to provide more conclusive evidence that the second intermediate is indeed a thiadioxirane. We report here the results of our studies on the photooxidations of sulfenamides (X = NR_2).

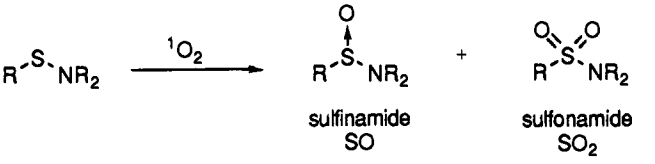
Results and Discussion

Sulfenamides **2**−**9** were synthesized by the procedure of Barton[11] (eq 2) using an excess of the amine in order to maintain a high pH and suppress disulfide formation which can occur by thiol attack on a protonated sulfenamide. Sulfenamide **10**

$$R_2NH \xrightarrow[(2)\ R_2NH,\ excess]{(1)\ NaOCl \atop (3)\ R'SH} R_2N{-}SR' \qquad (2)$$

was synthesized by addition of morpholine to 4-nitrobenzenesulfenyl chloride. All the sulfenamides were stable for extended periods of time except for **5**, which decomposed within a few minutes at room temperature. Photooxidations of the sulfenamides (0.05−0.1 M) were conducted in a variety of solvents containing (2−4) × 10^{-5} M sensitizer by irradiation with either a 500 or 650 W tungsten−halogen lamp. Filter solutions[12] were used in every case to insure that irradiation of the sulfenamide or it oxidation products did not occur.

Scheme 2



The photooxidations of **2**−**7** were monitored by ^{1}H NMR and the photooxidations of **8**−**10** by both ^{1}H NMR and GC/MS. The sulfinamides (Scheme 2) are the exclusive products (>98%) formed during the photooxidations of **2**−**6** as detected by ^{1}H NMR. Co-photooxidation and NMR monitoring of an independently synthesized sample of **2SO$_2$** and **2** demonstrate that under the reaction conditions the sulfonamide is stable and does not form two molecules of **2SO**. In addition, co-photooxidation of **3** and **6** did not lead to the formation of **2** or any oxidized derivative of **2**, demonstrating that cleavage of the S−N bond does not occur on the reaction surface.

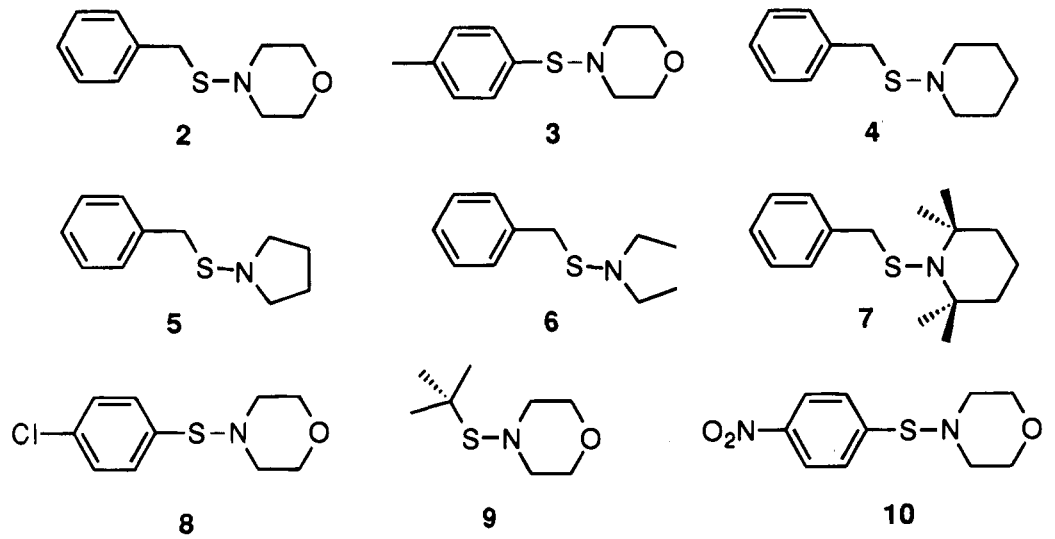
The photooxidations of **7**−**10**, however, are unique in that these sulfenamides react with singlet oxygen to give easily observable amounts of the sulfonamides. The formation of approximately 5% of the sulfonamide during the photooxidation of **7** is revealed in the NMR spectrum by the appearance of a small singlet at 4.27 ppm for the benzylic protons. The sulfinamide, **7SO**, and sulfonamide, **7SO$_2$**, are easily distinguishable since the benzylic protons are diastereotopic only in the sulfinamide and appear as a AB quartet as a result of the chiral center at sulfur.

The formation of the sulfonamide during the photooxidation of **8** was detected both by appearance of a pair of doublets in the aromatic region at 6.91 ppm (J = 8.3 Hz) and 7.29 ppm (J = 8.3 Hz) of the ^{1}H NMR and by GC/MS. The near identical

(10) Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Vol. 19, pp 408−483.

(11) Barton, D. H. R.; Hesse, R. H.; O'Sullivan, A. C.; Pechet, M. M. *J. Org. Chem.* **1991**, *56*, 6702−6704.

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



amounts of **8SO₂** measured by NMR (≈12%) and by GC/MS (12−16%) demonstrate the compatibility of both the sulfinamide and sulfonamide to the GC/MS conditions. Sulfonamide formation increased to approximately 20 and 25% during the photooxidations of **9** and **10**, respectively, as detected by GC/MS during the photooxidation of **9** and by both GC/MS and NMR (doublets at 7.62 and 8.21 ppm, J = 8 Hz) during the photooxidation of **10**.

Injections of pure samples of **9SO** and **8SO** onto the GC column demonstrates that the sulfonamides do not form by disproportionations of the sulfinamides under the GC conditions. In addition, spectral data and combustion analyses (see the Experimental Section) of purified samples of **8SO₂** and **9SO₂** are consistent with their assigned structures.

Diphenyl Sulfide and Sulfoxide Trapping Studies. Co-photooxidations of **2** with Ph_2SO and Ph_2S in benzene resulted in formations of the trapping products Ph_2SO_2 and Ph_2SO, respectively, despite the fact that the trapping agents themselves are inert to singlet oxygen under our reaction conditions. A quantitative trapping study with Ph_2SO (Scheme 1) obeys eq 3, which was derived in 1983 by Foote and co-workers[6] to

$$\frac{[\mathbf{2SO}]}{[Ph_2SO_2]} = 1 + \frac{2k_X}{k_{SO}[Ph_2SO]} \qquad (3)$$

describe the mechanistic proposal presented in Scheme 1. A plot (Figure 1) of $[\mathbf{2SO}]/[Ph_2SO_2]$ versus $1/[Ph_2SO]$ is linear with a slope which is independent of the concentrations of [**2**] consistent with a lack of a direct competition between Ph_2SO and **2** for a common intermediate. The value of k_X/k_{SO} derived from the slope of Figure 1 (0.068) is three times larger than the same value obtained from the analysis of Ph_2SO trapping data collected during the photooxidations of Et_2S.[6] It is clearly risky to base a mechanistic interpretation on a factor of 3 difference in k_X/k_{SO}; never-the-less, it is possible that the larger value for **2** reflects the more rapid interconversion of the persulfinamide **A** (Scheme 1; R = CH_2Ph, X = 4-morpholinyl) in comparison to the persulfoxide **A** (Scheme 1; R = X = Et) to the second intermediate ($k_X^{RSNR_2} > k_X^{R_2S}$). This analysis is based upon the assumption that the rate of abstraction, k_{SO}, of the remote pendant oxygen in the persulfinate intermediate (Scheme 1) by the Ph_2SO is insensitive to the identity of X.[13] Furthermore, it

(13) This speculation is based upon the fact that the group X is three atoms removed from the site of reactivity, the peroxy anion. It is likely however that a small through-bond and through-space effect does operate to disperse the negative charge when X is electron withdrawing. This would also have the effect of making k_{SO} smaller and k_X/k_{SO} larger as observed.

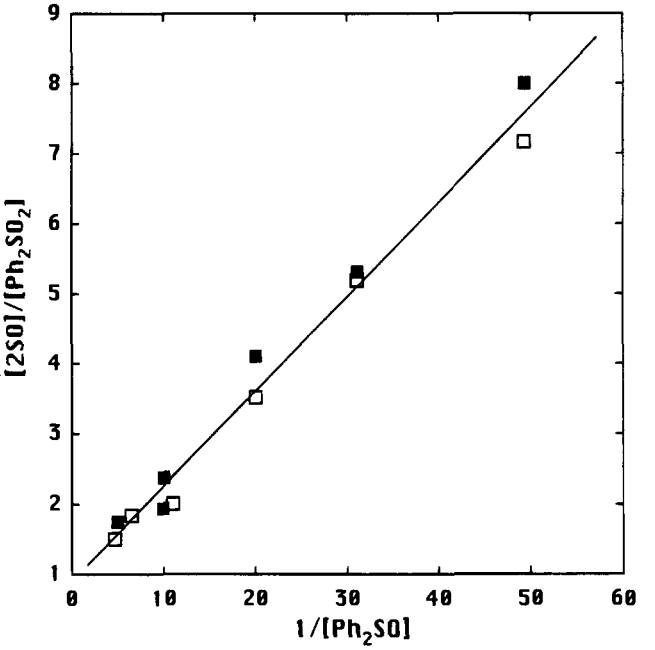


Figure 1. Trapping of an intermediate in the photooxidation of **2** with Ph_2SO in benzene: ■, 0.2 M; □, 0.1 M. Slope = 0.14, r = 0.9918.

is tempting to suggest that this provides evidence that the second intermediate is the three-membered ring thiadioxirane (Scheme 1; R = CH_2Ph, X = 4-morpholinyl) since the larger value reflects the increased stability of the thiadioxirane as a result of the greater electronegativity of nitrogen in comparison to carbon.[10]

In contrast to the results in benzene, a quantitative treatment (Figure 2) of the trapping with Ph_2SO in methanol demonstrates that the slope is a function of [**2**] as predicted by eq 4 and

$$\frac{[\mathbf{2SO}]}{[Ph_2SO_2]} = 1 + \frac{2k_{SO}[2]}{k_{PhO}[Ph_2SO]} \qquad (4)$$

Scheme 3. The *sensitivity* of the slope to the concentrations of **2** (Figure 2) is consistent with direct competition between **2** and Ph_2SO for a common intermediate. We suggest that in methanol the persulfoxide intermediate is rapidly converted to a sulfurane, **11**, which is the kinetically detected intermediate. Consistent with this suggestion is our recently published

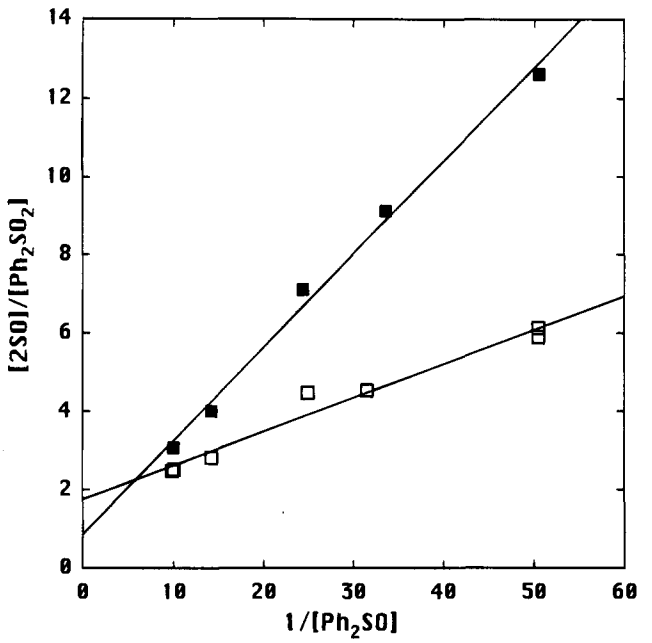


Figure 2. Trapping of an intermediate in the photooxidation of **2** with Ph_2SO in methanol: ■, 0.5 M (slope = 0.87, r = 0.9854); □, 0.1 M (slope 0.24, r = 0.9964).

work[14-16] in which we took advantage of the Thorpe Ingold effect to demonstrate with the aid of oxygen isotopic labeling that a tethered hydroxy group intramolecularly adds to a persulfoxide intermediate to form a novel hydroperoxy sulfurane. The magnitude of k_{SO}/k_{PhO} (Scheme 3; 1.03 ± 0.16) is considerably smaller than the value derived in the photooxidations of Et_2S (2.77 ± 0.5), which we suggest reflects the greater nucleophilicity of Et_2S in comparison to **2**.[17] The difference in nucleophilicity is undoubtably also responsible for the smaller k_T value for the photooxidation of **2** in comparison to the value reported for Et_2S (vide infra).

A quantitative study of Ph_2S trapping in benzene (Figure 3) demonstrates that it obeys eq 5 and is consistent with competi-

$$\frac{[\mathbf{2SO}]}{[Ph_2SO]} = 1 + \frac{2k_S[2]}{k_{PhS}[Ph_2S]} \qquad (5)$$

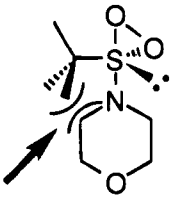
tive trapping of a common intermediate by Ph_2S and **2** and further supports the mechanistic proposal which invokes two intermediates (Scheme 1). The value of k_S/k_{PhS} derived from the slopes of the lines in Figure 3 (1.88) is nearly 1 order of magnitude smaller than the k_S/k_{PhS} value (17.63) reported for trapping during the photooxidations of Et_2S. Changing the X group in the thiadioxirane (Scheme 1) from carbon to nitrogen will undoubtably change the electronic character of both oxygens and affect both k_S and k_{PhS}. However, since this change should affect both rate constants to the same extent, it is reasonable to suggest that the smaller value of k_S/k_{PhS} observed in the photooxidations of **2** reflects the decreased nucleophilicity of **2** in comparison to Et_2S.

Having established the presence of two intermediates on the sulfenamide **2** photooxidation surface, we next turned our attention to a determination of the electronic character of these intermediates. This was accomplished by a Hammett trapping study using para-substituted aryl sulfides and sulfoxides (Table 1) The sulfoxides trapped a nucleophilic intermediate as revealed by a ρ^0 value of +1.3 and the sulfides an electrophilic intermediate as indicated by a ρ^+ of −0.26.

Oxygen Isotopic Labeling Experiments. Within the framework of the two intermediate mechanism (Scheme 1), there are two mechanistic possibilities for the formations of the sulfonamides during the photooxidations of **7**−**10**: (1) unimolecular cleavage of the thiadioxirane or (2) bimolecular trapping of the persulfinamide by adventitious sulfinamide formed in the reaction. The two possibilities differ in the origin of the two oxygen atoms that were introduced to form the sulfonamide. Unimolecular decomposition of the thiadioxirane requires that both oxygen atoms come from the same oxygen molecule while bimolecular trapping requires different molecular ancestry for these atoms.

In order to differentiate between these two mechanistic possibilities, the photooxidations of **8** and **9** were examined in the presence of a mixture of $^{32}O_2$ and $^{36}O_2$ and the isotopic composition of the sulfonamide products measured by GC/MS. The $M/(M+2)/(M+4)$ ratios for these experiments are listed in Table 2 along with the calculated values for both the unimolecular and bimolecular mechanisms. These results demonstrate that the sulfonamides in both cases are formed by bimolecular trapping of the persulfinamides.[1]

The formation of the sulfonamide during the photooxidation of **8** but its complete absence during the photooxidation of **3** can be attributed to the enhanced electrophilicity of **8SO** in comparison to **3SO** as a result of the *p*-chloro substituent. However, the same explanation applied to the photooxidation of **9** is unpalatable since **9SO** is unlikely on both steric and electronic grounds to be a better trapping agent than any of the sulfinamides formed in the reactions of **2**−**6**, which do not form sulfonamide products. As an alternative explanation, we suggest that the unexpected ability of **9SO** to bimolecularly remove an oxygen atom from the persulfinamide reflects a decrease in the competing rate constant, k_X (Scheme 1), as a result of destabilizing steric interactions in the thiadioxirane, **12**.



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Photooxidation Kinetics. The suggestion that k_X in the reaction of **9** is smaller than in the photooxidations of less sterically hindered sulfenamides allowing trapping, k_{SO}, to compete leads to the prediction that physical quenching, k_q (Scheme 1), should also be more important in the photooxidation of **9**. In order to examine this possibility, we have measured and compared the rate constants for substrate-induced removal of $^1O_2$, k_T, and the rate constants for product formation, k_r, for photooxidations of **2** and **9**. These data are presented and compared in Table 3 to similar data collected for a disulfide, a sulfenate ester, and several sulfenamides and sulfides. These experimentally derived rate constants and eq 6 are used to calculate k_q, the rate constant for physical quenching.

$$k_T = ak_r + k_q \qquad (6)$$

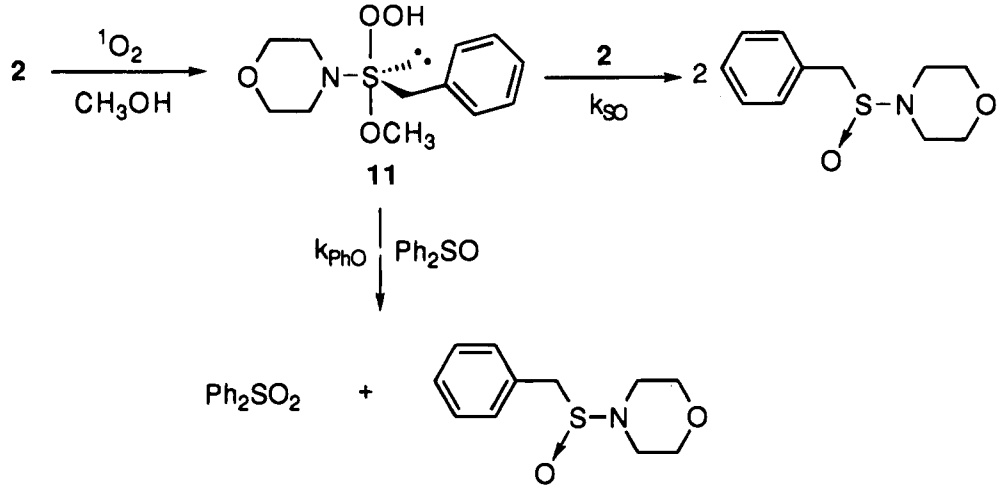
(14) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044−4046.

(15) Clennan, E. L.; Yang, K.; Chen, X. *J. Org. Chem.* **1991**, *56*, 5251−5252.

(16) Clennan, E. L.; Yang, K. *J. Org. Chem.* **1992**, *57*, 4477−4487.

(17) Disulfides are also weaker nucleophiles than dialkyl sulfides. Kice, J. L. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1980; Vol. 17, pp 65−181.

Scheme 3



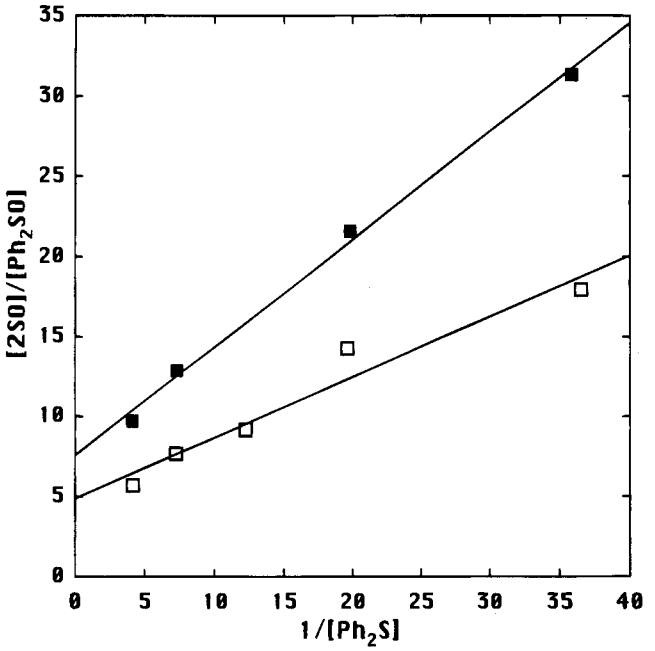


Figure 3. Trapping of an intermediate in the photooxidation of **2** with Ph_2S in benzene: ■, 0.2 M (slope = 0.68, r = 0.999); □ 0.1 M (slope = 0.38, r = 0.973).

Table 1. Hammett Trapping Studies Using Diaryl Sulfides and Sulfoxides in the Photooxidations of 2[a]

X	k_X/k_H	$\log(k_X/k_H)$	$\Sigma\sigma^{0\,b}$
	Diaryl Sulfoxide Trapping $(XC_6H_4)_2SO$[c]		
OMe	0.80	−0.0969	−0.24
Me	0.72	−0.1427	−0.28
H	1	0	0
Cl	12.2	1.086	+0.68
	Diaryl Sulfide Trapping $(XC_6H_4)_2S$[d]		
OMe	2.5	0.3979	−1.56
Me	1.25	0.0969	−0.60
H	1	0	0

[a] In benzene. [b] Sigma values from Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: Essex, England, 1987; p 134. [c] ϱ^0 = +1.3, r = 0.9833. [d] ϱ^+ = −0.26, r = 0.9879.

The total rate constants, k_T, which represents a composite of all chemical, k_r, and physical, k_q, channels of singlet oxygen deactivation induced by the sulfenamides were measured in benzene by monitoring their ability to quench singlet oxygen emission at 1270 nm.[18,19] Singlet oxygen reacts with sulfenamide **2** approximately 10 times slower than with Et_2S and 3.7 times faster than with phenyl ethylsulfenate (Table 3). This trend is that expected based upon the known electrophilic character of $^1O_2$ and the nucleophilicity of the sulfur atom in RSX as predicted by the electronegativity of X. The electronegativity of the X group, however, cannot be the sole determinant of reactivity since dimethyl disulfide reacts much slower than **2** despite the greater electronegativity of nitrogen in comparison to sulfur. A comparison of the k_T values for **2** and **9** demonstrates that steric effects which have also been observed in sulfide photooxidations[20,21] play a role in determining sulfenamide reactivity.

The k_r values in Table 3 were determined using eq 7 which was developed by Higgins, Foote, and Cheng to describe the relative rate constants for competitive removal of singlet oxygen from solution by two substrates.[22] The relative rate constant

$$\frac{k_r(\text{substrate})}{k_r(\text{olefin})} = \frac{\log([\text{substrate}]_f/[\text{substrate}]_o)}{\log([\text{olefin}]_f/[\text{olefin}]_o)} \qquad (7)$$

for the reaction of **2** was measured in benzene in competition with adamantylideneadamantane (k_T = 3.49 × 10^5 M^{-1} s^{-1}) and octalin (k_T = 1.84 × 10^6 M^{-1} s^{-1}), for **9** (Figure 4) in competition with α-pinene (k_T = 4.34 × 10^4 M^{-1} s^{-1}), and for pentamethylene sulfide ($(CH_2)_5S$) in acetone in competition with tetramethylethylene (k_T = 1.2 × 10^7 M^{-1} s^{-1}). The absence of a physical quenching component in the interaction of singlet oxygen with several isolated olefins has previously been demonstrated, allowing the absolute values of the chemical rate constants for the sulfide and sulfenamides to be determined by setting k_T(olefin) = k_r(olefin).[23] Remarkably, in contrast to the k_T values, the rate constant k_r for sulfenamide **2** is actually six times larger than k_r for pentamethylene sulfide. A steric effect on k_r is also apparent from a comparison of the k_r values for **2** and **9**.

In order to convert these experimentally derived rate constants to k_q and ultimately the percent of physical quenching (%PQ = k_q/k_T × 100), the value of a in eq 6 must be evaluated. In

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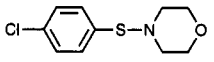
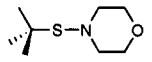
(21) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765–769.
(22) Higgins, R.; Foote, C. S.; Cheng, H. In *Advances in Chemistry Series, Vol. 77*; Gould, R. F., Ed.; American Chemical Society: Washington DC, 1968; pp 102–117.
(23) Manring, L. E.; Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4707–4710.

Table 2. Oxygen Labeling Studies[a]

compd[b,c]	oxygen isotopic contribution to M	$M+2$	$M+4$	%UM[e]	%BM[d]
	1.753	2.648	1		100
	1.324	0	1	100	
 **8**	1.79 ± 0.05	2.67 ± 0.04	1		100 ± 2
 **9**	1.75 ± 0.07	2.60 ± 0.05	1		98 ± 2

[a] In benzene using 5×10^{-5} M TPP as the sensitizer. [b] Percent conversions: **8**, 100%; **9**, 100%. [c] The $^{32}O_2/^{36}O_2$ (*X*/*Y*) ratio of oxygen gas was 1.324:1 and was verified in each experiment by monitoring the $RS^{16}OX/RS^{18}OX$ ratios. [d] Percent of bimolecular formation of the sulfonyl product. (%BM = $f_{BM} \times 100$ and $f_{BM} = (M+2)/[(2(1.324)) \times (M+4)]$). See the Experimental Section for details. [e] Percent of unimolecular formation of the sulfonyl product (%UM = 100 − %BM).

Table 3. Photooxidation Kinetics

Compd	$k_T \times 10^{-4}$ (M^{-1} s^{-1})	$k_r \times 10^{-4}$ (M^{-1} s^{-1})	$k_q \times 10^{-4}$ (M^{-1} s^{-1})	%PQ[a]
2	128	294	*b*	0
4	355			
6	196			
7	77.1			
8	15.8			
9	4.04	3.75	2.0 (±0.4)	45−55
$(CH_2)_5S$	1480	47	1433	97
Et_2S	1710			>95[e]
MeSSMe[c]	51.8	3.38	48.4	>93
$PhSOCH_2CH_3$[d]	34.6			

[a] %PQ = percent of physical quenching. [b] Too small to measure. [c] Wang, D.; Clennan, E. L. Unpublished results. [d] Zhang, H.; Chen, M. F.; Clennan, E. L. Unpublished results. [e] Reference 6.

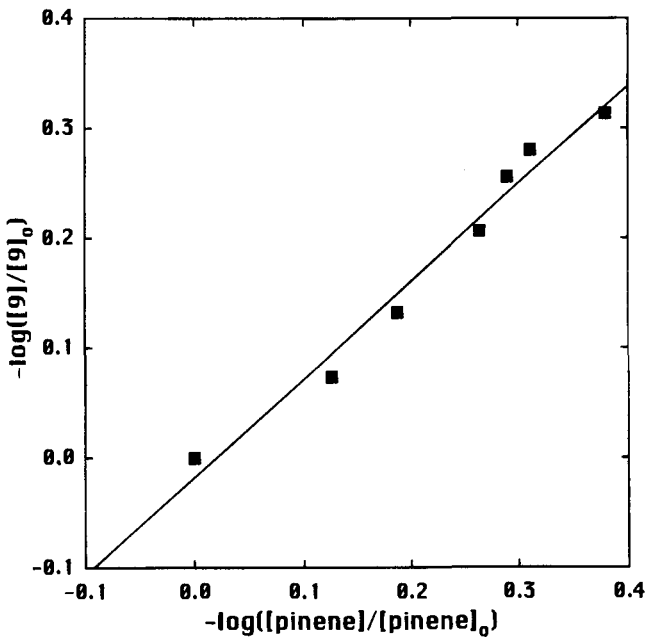
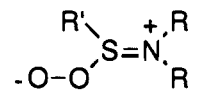


Figure 4. Competitive photooxidation of **9** and pinene. Slope = 0.87, $r = 0.9825$.

the photooxidation of **2**, the value of *a* is 0.5 since only sulfinamide ($RSONR_2$) is formed and as a result two products are formed for every $^1O_2$ molecule that disappears. At the other extreme, the value of *a* would be 1.0 for a photooxidation that produces only sulfonamide (RSO_2NR_2). Since the concentration of sulfonamide increases with increasing conversion of starting material, the value of *a* can vary from 0.5 to 1.0 depending on the extent of reaction. In the photooxidation of **9** at 100% conversion to product, only 20% of the sulfonamide is formed so that *a* will be between 0.5 and 0.6 ([0.5 × 0.8] + [1.0 × 0.2]), which is reflected in the uncertainty (± value) reported in Table 2 for the k_q rate constant.

The rate constant for physical quenching, k_q, could not be determined for the photooxidation of **2** since it is so small relative to k_r, and as a consequence, the percent of physical quenching is approximately zero. For comparison, the percent of physical quenching is greater than 93−95% for diethyl sulfide,[6] dimethyl disulfide,[24] and pentamethylene sulfide[25] (Table 3). *It is remarkable that a molecule which is part amine and part sulfide, both notorious physical quenchers of singlet oxygen, has no physical quenching component.*[26,27]

The S−O bond in the persulfinamide is likely to be shorter than in the persulfoxide as a result of the increased s-character acquired when nitrogen acts as a π-donor (intermediate **13**; **A**



13

in Scheme 1). Consequently, we suggest that k_q will be suppressed in the sulfenamides relative to the sulfides, reflecting a stronger S−O bond; however, detailed calculations will be necessary in order to determine the validity of this suggestion. This explanation is not inconsistent with with our suggestion that the smaller k_T's for sulfenamides reflect destabilization of the persulfinamide relative to diethyl persulfoxide ($Et_2S^+OO^-$) but is just an indication that in these intermediates σ-withdrawal by nitrogen is more important than its ability to act as a π-donor.

In contrast to the results observed with **2**, the 45−55% physical quenching observed in the photooxidation of **9** corroborates our earlier suggestion (vide supra) that k_X(**9**) is slow in comparison to k_X(**2**), allowing both trapping and physical quenching to compete. A steric interaction between R and R′ in **13** (R′ = *tert*-butyl, R = 4-morpholinyl) would lead to an increase in the R'SNR dihedral angle, a decrease in the s character and in the strength of the S−O bond, and an increase in physical quenching. However, this alternative mechanism

(24) Clennan, E. L.; Wang, D. Unpublished results.
(25) Clennan, E. L.; Oolman, K. A.; Yang, K.; Wang, D.-X. *J. Org. Chem.* **1991**, *56*, 4286−4289.
(26) Épshtein, L. M.; Zhdanova, A. N.; Khazanova, Y. A.; Fel'dshtein, M. S.; Kazitsyna, L. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 87−89.
(27) Épshtein and co-workers have noted a similar phenomenon during a study of the hydrogen-bonding ability of sulfenamides and pointed out that "the adjacency of two identical or different heteroatoms results in complicated electronic interactions which appreciably changes the donor properties of a bidentate base relative to a monodentate one." Épshtein, L. M.; Zhdanova, A. N.; Dolgopyat, N. S.; Bochvar, D. A.; Gambaryan, N. P.; Kazitsyna, L. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2487−2493.

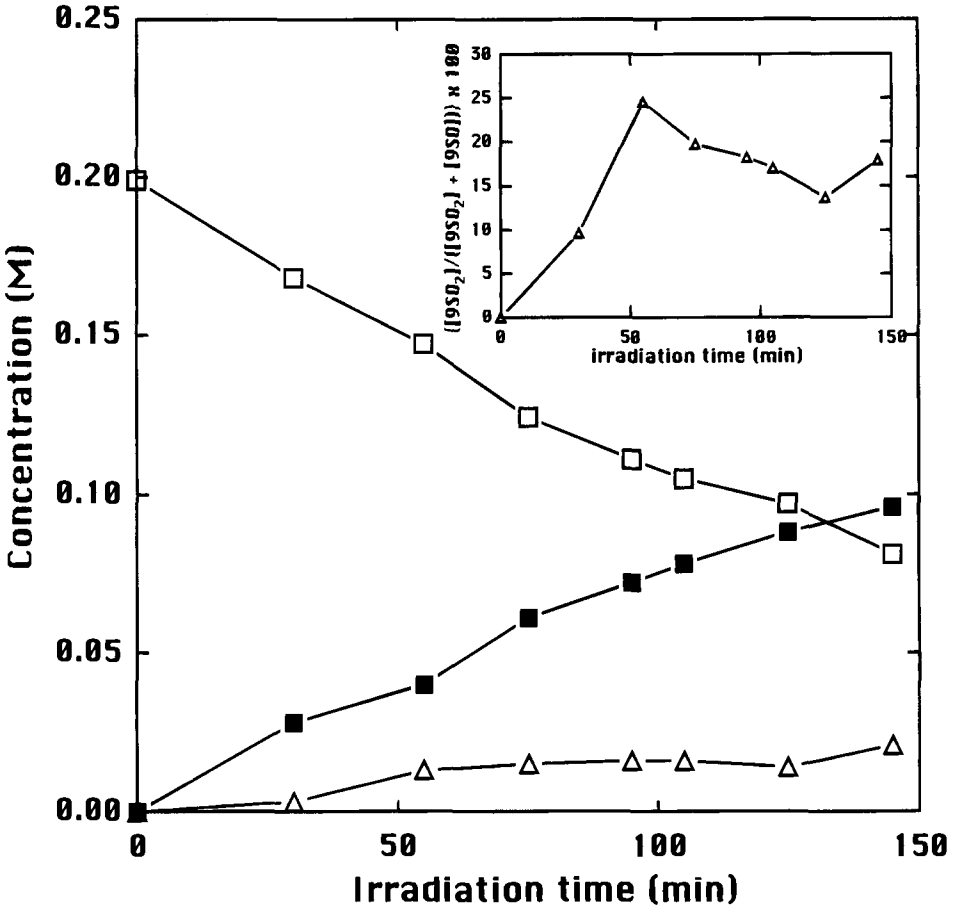


Figure 5. Reaction profile for the photooxidation of **9**: □, **9**; ■, **9SO**; △, $\mathbf{9SO_2}$.

while providing an explanation for the trend in k_q does not provide a satisfactory rationale for the enhanced trapping with **9SO**.

Reaction Profile for the Photooxidation of 9. The formation of **9SO** steadily increased as a function of photolysis time as depicted in Figure 5. In contrast, the formation of the sulfonamide, $\mathbf{9SO_2}$, reached a plateau at approximately 60 min. This can be most easily visualized by examining the percent of $\mathbf{9SO_2}$ ($([\mathbf{9SO_2}] \times 100)/([\mathbf{9SO_2}] + [\mathbf{9SO}])$) as a function of photolysis time (inset in Figure 5). This result appears to be inconsistent with the oxygen labeling results (vide supra) which concluded that $\mathbf{9SO_2}$ is formed exclusively by trapping of the persulfinamide intermediate with **9SO**. This trapping mechanism requires an increase in $\mathbf{9SO_2}$ formation as more trapping agent, **9SO**, is formed. This is especially true since the competing trapping reaction with **9** becomes less important as its concentration decreases with reaction time.

In order to rationalize these apparently conflicting results, we point out that sulfone formation is remarkably sensitive to the presence of small amounts of methanol and presumably to traces of hydrogen peroxide, which is invariably formed in these reactions.[28] As the concentration of methanol in toluene exceeds 0.5%, it dramatically shuts off sulfone formation in the photooxidation of phenyl butyl sulfide (Figure 6). Consequently this phenomenon provides an explanation for the data presented in Figure 5 and also for Sawaki's observation[7] that the sulfone/sulfoxide ratio decreases as a function of time.

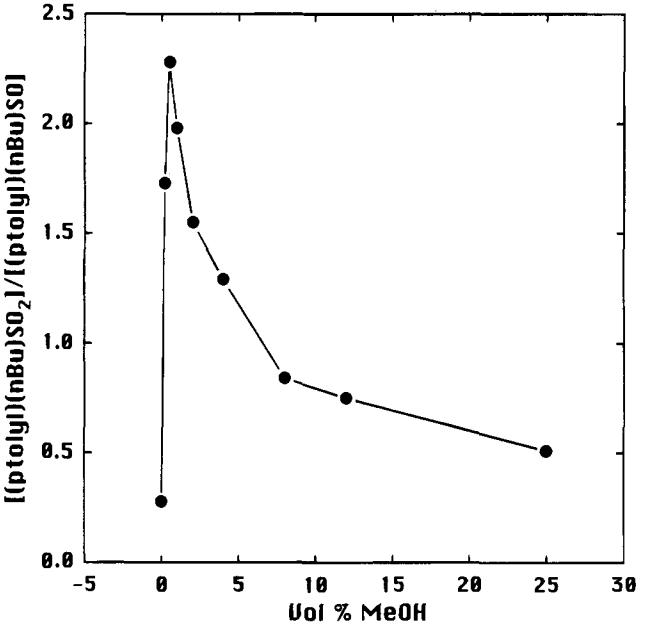


Figure 6. Sulfone/sulfoxide ratio in the photooxidation of 2×10^{-2} M *p*-tolyl *n*-butyl sulfide at −72 °C in toluene doped with methanol.

Conclusion

The reaction surface describing the interaction of singlet oxygen with sulfenamides is remarkably similar to the analogous surface for the reaction of diethyl sulfide. In particular, (1) in both reactions two kinetically distinguishable intermediates are observed in benzene but only one is required in methanol and (2) the initially formed intermediates in both systems react as nucleophiles with Ph_2SO while the subsequently formed intermediates react as electrophiles with Ph_2S. On the other hand, the reactions of sulfenamides exhibit unique characteristics, most notably the dominance of chemical rather than physical reactivity toward singlet oxygen.

(28) Clennan, E. L.; Yang, K. *Tetrahedron Lett.* **1993**, *34*, 1697−1700.

The electronic characteristics of the intermediates are consistent with the anticipated behavior for a persulfinamide and thiadioxirane. Circumstantial evidence for assignment of a thiadioxirane structure to the second intermediate includes the tenuous suggestion that the 3-fold larger k_X/k_{SO} observed in the photooxidations of **2** in comparison to Et_2S reflects the ability of nitrogen to adopt an apical position and to stabilize this trigonal bipyramidal intermediate. More concrete evidence, however, for a thiadioxirane structure is the observation of physical quenching by **9** which argues that the second intermediate is sensitive to steric interactions. A pronounced sensitivity to steric effects is anticipated in a pseudo trigonal bipyramidal thiadioxirane in which the angle between an equatorial and apical ligand approaches 90°.

Experimental Section

General Aspects. Proton and carbon NMR were obtained either on a JEOL GX 270 or 400 MHz NMR and are referenced internally to TMS. The GC/MS were collected on a Hewlett Packard instrument consisting of a 5890 series II GC and a 5971 series mass selective detector. All reactions were analyzed on a HP-5 30 m × 0.25 mm × 0.25 μm (length × inside diameter × film thickness) capillary GC column using helium as the carrier gas. HPLC analyses were done on a Hewlett Packard 1090 equipped with a diode array detector using a HP DDS hypersil microbore column (100 × 2.1 mm).

Thiophenol, *p*-chlorothiophenol, 2-methyl-2-propanethiol, gold label morpholine, $\Delta^{9,10}$-octalin, (1*R*)-(+)-α-pinene, diethylamine, piperidine, pyrrolidine, 2,2,6,6-tetramethylpiperidine, benzyl mercaptan, *tert*-butyl mercaptan, *p*-thiocresol, and 4-nitrobenzenesulfenyl chloride were obtained from Aldrich and used as received. 1,2-Dimethoxyethane was obtained from Eastman Kodak and used without further purification. Sodium sulfite was obtained from Baker and magnesium sulfate from Spectrum Chemical Mfg. Corp. and used as received. Biphenyl (Aldrich, 99+%) and 4-*tert*-butylcyclohexanone (Aldrich, 99%) were recrystallized from hexanes. The oxygen gas was custom mixed by ICON Services Inc. Combustion analysis were obtained from Atlantic Microlabs Inc. in Norcross, GA. High-resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry in Lincoln, NE.

4-Morpholinyl Benzyl Sulfide (2) was synthesized by the method of Barton[11] in 85% yield and purified by two recrystallizations from hexanes. ^{1}H NMR ($CDCl_3$): δ 2.94 (t, *J* = 4.6 Hz, 4H), 3.62 (t, *J* = 4.6 Hz, 4H), 3.93 (s, 2H), 7.2−7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 36.86, 56.25, 67.57, 126.83, 128.45, 129.25, 137.50.

4-Morpholinyl Benzyl Sulfoxide (2SO)[29] was synthesized in 75% yield by taking 2.4 mmol of the sulfenamide, **2**, in 10 mL of $CHCl_3$ in a 100 mL flask and adding dropwise 2.5 mmol of MCPBA dissolved in 20 mL of $CHCl_3$ over a 1 h period at room temperature. The reaction mixture was allowed to stir for an additional 2 h, and then ammonia gas was bubbled through the mixture, resulting in immediate formation of a white solid which was removed after a period of 2 h by gravity filtration. The solvent was then removed by rotary evaporation and the product purified by two recrystallizations from methylene chloride/hexanes. ^{1}H NMR ($CDCl_3$): δ 3.04−3.14 (m, 2H), 3.14−3.26 (m, 2H), 3.68−3.74 (m, 4H), 4.03 (AB quartet, *J* = 12 Hz, 2H). ^{1}H NMR (acetone-d_6): δ 2.97−3.02 (m, 2H), 3.16−3.21 (m, 2H), 3.61−3.71 (m, 4H), 4.01 (d, *J* = 13.2 Hz, 1H), 4.13 (d, *J* = 13.2 Hz, 1H), 7.29−7.37 (m, 5H). ^{13}C NMR (acetone-d_6): δ 46.33, 59.05, 67.32, 128.42, 129.34, 131.08, 132.68.

4-Morpholinyl Benzyl Sulfone ($2SO_2$) was synthesized in 82% yield by the method of Larsen.[30] Mp: 172−174 °C. ^{1}H NMR (acetone-d_6) δ 3.13−3.16 (m, 4H), 3.59−3.61 (m, 4H), 4.37 (s, 2H), 7.38−7.40 (m, 3H), 7.47−7.49 (m, 2H). MS: *m/e* 241 ($M^{\bullet+}$, 4.5%), 242 (0.6%), 243 (0.3%), 91 (100%), 86 (17.5%). Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80. Found: C, 54.56; H, 6.30, N, 5.89.

4-Morpholinyl *p*-Methylphenyl Sulfide (3) was synthesized by the method of Barton[11] and purified by recrystallization from hexanes. ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 3H), 2.87−2.91 (m, 4H), 3.67−3.71 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 21.20, 55.82, 67.58, 129.03, 129.38, 133.11, 138.92. MS: *m/e* 209($M^{\bullet+}$, 100%), 210 (13.8%), 211 (5.4%), 151 (24.4%), 123 (53.3%), 86 (43.4%), 56 (45.4%).

4-Morpholinyl *p*-Methylphenyl Sulfoxide (3SO). ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 3H), 2.94−3.00 (m, 2H), 3.12−3.19 (m, 2H), 3.64−3.78 (m, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H).

1-Piperidinyl Benzyl Sulfide (4) was synthesized by the method of Barton[11] and purified at reduced pressure by Kugelrohr distillation. ^{1}H NMR (acetone-d_6): δ 1.35−1.37 (m, 2H), 1.52−1.58 (m, 4H), 2.96 (t, *J* = 5.3 Hz, 4H), 3.93 (s, 2H), 7.21−7.34 (m, 5H). MS: *m/e* 207 ($M^{\bullet+}$, 41%), 208 (5.5%), 209 (2.0%), 116 (16.5%), 91 (100%). HR EIMS: calcd for $C_{12}H_{17}NS$ *m/e* 207.1083, found 207.1082.

1-Piperidinyl Benzyl Sulfoxide (4SO). ^{1}H NMR ($CDCl_3$): δ 1.56−1.59 (m, 6H), 2.97−3.14 (m, 2H), 3.15−3.20 (m, 2H), 3.97 (d, *J* = 12.9 Hz, 1H), 4.03 (d, *J* = 12.9 Hz, 1H), 7.25−7.37 (m, 5H).

1-Pyrrolidinyl Benzyl Sulfide (5) was synthesized by the method of Barton.[11] The large amount of dibenzyl disulfide byproduct was separated from the product by crystallization at −12 °C in 1:5 H_2O/EtOH. Final purification was accomplished by Kugelrohr distillation at 55 °C/(0.6 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.73−1.78 (m, 4H), 2.96−3.01 (m, 4H), 3.88 (s, 2H), 7.21−7.34 (m, 5H).

1-Pyrrolidinyl Benzyl Sulfoxide (5SO). ^{1}H NMR ($CDCl_3$): δ 1.84−2.2 (m, 4H), 3.16−3.22 (m, 2H), 3.41−3.47 (m, 2H), 3.91 (d, *J* = 12.9 Hz, 1H), 4.07 (d, *J* = 12.9 Hz, 1H), 7.26−7.38 (m, 5H).

1-Diethylaminyl Benzyl Sulfide (6) was synthesized by the method of Barton[11] and purified by Kugelrohr distillation at 55 °C/(0.6 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.12 (t, *J* = 6.9 Hz, 6H), 2.86 (q, *J* = 7.0 Hz, 4H), 3.79 (s, 2H), 7.23−7.30 (m, 5H). MS: *m/e* 195 ($M^{\bullet+}$, 35.4%), 196 (4.5%), 197 (1.8%), 180 (2.8%), 123 (10.8%), 104 (10.1%), 91 (100%).

1-Diethylaminyl Benzyl Sulfoxide (6SO). ^{1}H NMR (acetone-d_6): δ 1.06 (t, *J* = 7.3 Hz, 6H), 3.07 (dq, *J* = 13.9, 7.3 Hz, 2H), 3.22 (dq, *J* = 13.9, 7.3 Hz, 2H), 3.93 (d, *J* = 12.9 Hz, 1H), 4.01 (d, *J* = 12.9 Hz, 1H), 7.31−7.34 (m, 5H).

2,2,6,6-Tetramethyl-1-piperidinyl Benzyl Sulfide (7) was synthesized by the method of Barton[11] and purified by preparative thin layer chromatography on silica gel with elution by 1:4 ethyl acetate/hexanes. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 6H), 1.37 (s, 6H), 1.44−1.58 (m, 6H), 3.83 (s, 2H), 7.20−7.28 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 17.37 (t, *J* = 129 Hz), 24.31 (q, *J* = 126 Hz), 33.75 (q, *J* = 126 Hz), 40.85 (t, *J* = 128 Hz), 49.02 (t, *J* = 142 Hz), 59.45 (s), 126.92 (d, *J* = 165 Hz), 128.34 (d, *J* = 160 Hz), 129.32 (d, *J* = 160 Hz), 136.24 (s). MS: *m/e* 263 ($M^{\bullet+}$, 23.8%), 264 (4.3%), 265 (1.4%), 248 (100%), 123 (21.1%), 91 (52.5%).

4-Morpholinyl *p*-Chlorophenyl Sulfide (8) was synthesized in 14% yield by the method of Barton[11] and purified using a chromatotron on a silica plate. ^{1}H NMR ($CDCl_3$): δ 2.92−2.96 (m, 4H), 3.70−3.73 (m, 4H), 7.31−7.40 (m, 4H). MS: *m/e* 229 ($M^{\bullet+}$, 100%), 230 (13%), 231 (36.7%), 232 (4.1%), 233 (1.8%), 171 (32.9%), 143 (56%), 108 (41.3%), 86 (58%), 56 (83.8%).

4-Morpholinyl *p*-Chlorophenyl Sulfoxide (8SO) was synthesized in 80% yield by taking 2.4 mmol of the sulfenamide, **8**, in 10 mL of $CHCl_3$ in a 100 mL flask and adding dropwise 2.5 mmol of MCPBA dissolved in 20 mL of $CHCl_3$ over a 1 h period at room temperature. The reaction mixture was allowed to stir for an additional 2 h, and then ammonia gas was bubbled through the mixture, resulting in immediate formation of a white solid which was removed after a period of 2 h by gravity filtration. The solvent was then removed by rotary evaporation and the product purified by two recrystallizations from methylene chloride/hexanes. ^{1}H NMR (benzene-d_6): δ 2.60 (m, 2H), 2.78 (m, 2H), 3.31−3.33 (m, 4H), 7.09−7.1 (brn, 2H), 7.38 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (benzene-d_6): δ 45.97, 66.73, 128.00 (overlapped with benzene peak), 129.2, 137.18, 142.42. MS: *m/e* 245 ($M^{\bullet+}$, 4.0%), 246 (0.55%), 247 (1.4%), 197 (40.5%), 159 (17%), 86 (48.3%), 56 (100%). HR EIMS: calcd for $C_{10}H_{12}ClNO_2S$ *m/e* 245.02786, found 245.02796.

4-Morpholinyl *p*-Chlorophenyl Sulfone ($8SO_2$) was synthesized in 62% yield by the method of Larsen.[30] Mp: 146−147 °C. ^{1}H NMR (benzene-d_6): δ 2.51−2.55 (m, 4H), 3.21−3.25 (m, 4H), 6.95 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (benzene-d_6): δ 46.04, 65.81, 129.25, 129.48, 134.54, 139.08. MS: *m/e* 261 ($M^{\bullet+}$,

(29) Harpp, D. N.; G., B. T. *J. Org. Chem.* **1973**, *38*, 4328−4334.
(30) Larsen, R. D.; Roberts, F. E. *Synth. Commun.* **1986**, *16*, 899−903.

15.3%), 263 (6.4%), 175 (25.5%), 111 (32.6%), 86 (100%), 56 (62.0%). Anal. Calcd for $C_{10}H_{12}ClNO_3S$: C, 45.89; H, 4.62; N, 5.35. Found: C, 45.89; H, 4.67; N, 5.36.

4-Morpholinyl *tert*-Butyl Sulfide (9) was synthesized by the method of Barton[11] in 80% yield and purified on neutral alumina. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H), 2.96−3.00 (m, 4H), 3.67−3.70 (m, 4H). MS: *m/e* 175 ($M^{\bullet+}$, 33.1%), 176 (3.5%), 177 (1.6%), 119 (100%).

4-Morpholinyl *tert*-Butyl Sulfoxide (9SO) was synthesized in 70% yield by taking 2.4 mmol of the sulfenamide, **9**, in 10 mL of $CHCl_3$ in a 100 mL flask and adding dropwise 2.5 mmol of MCPBA dissolved in 20 mL of $CHCl_3$ over a 1 h period at room temperature. The reaction mixture was allowed to stir for an additional 2 h and then ammonia gas was bubbled through the mixture, resulting in immediate formation of a white solid which was removed after a period of 2 h by gravity filtration. The solvent was then removed by rotary evaporation, and the product purified by two recrystallizations from methylene chloride/hexanes. MS: *m/e* 191 ($M^{\bullet+}$, 4.1%), 135 (58%), 87 (100%), 57 (41.5%).

4-Morpholinyl *tert*-Butyl Sulfone ($9SO_2$) was synthesized in 70% yield by the method of Larsen.[30] Mp: 144−145 °C. MS: *m/e* 207 ($M^{\bullet+}$, 11.3%), 151 (5.3%), 128 (13.5%), 87 (57.8%), 86 (28.7%), 57 (100%). Anal. Calcd for $C_8H_{17}NO_3S$: C, 46.35; H, 8.27; N, 6.76. Found: C, 46.26; H, 8.21; N, 6.78.

4-Morpholinyl *p*-Nitrophenyl Sulfide (10). Dry CCl_4 (1 mL) and 6 g (25 mmol) of morpholine were added under a nitrogen atmosphere to a predried 150 mL three-neck flask equipped with an addition funnel containing 0.09 g (0.5 mmol) of 4-nitrobenzenesulfenyl chloride dissolved in 10 mL of P_2O_5 dried and freshly distilled CCl_4. The sulfenyl chloride solution was added to the flask over a period of 1 h with stirring, and the reaction was continued for another 1 h after the addition was complete. The resulting mixture was washed three times with a total of 100 mL of water and then dried over $MgSO_4$. The solvent was removed and the residue recrystallized three times from ethyl acetate/hexanes (1:3) to afford 0.03 g of analytically pure product. ^{1}H NMR (benzene-d_6): δ 2.63−2.65 (m, 4H), 3.38−3.40 (m, 4H), 6.93 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 7.9 Hz, 2H). ^{13}C NMR (benzene-d_6): δ 56.25, 67.52, 122.94, 124.08, 145.86, 149.52. MS: *m/e* 240 ($M^{\bullet+}$, 100%), 241 (13.3%), 242 (5.4%), 182 (20.2%), 86 (34.6%), 56 (53.8%).

4-Morpholinyl *p*-Nitrophenyl Sulfoxide (10SO) was synthesized in 60% yield by taking 2.4 mmol of the sulfenamide, **10**, in 10 mL of $CHCl_3$ in a 100 mL flask and adding dropwise 2.5 mmol of MCPBA dissolved in 20 mL of $CHCl_3$ over a 1 h period at room temperature. The reaction mixture was allowed to stir for an additional 2 h and then ammonia gas was bubbled through the mixture, resulting in immediate formation of a white solid which was removed after a period of 2 h by gravity filtration. The solvent was then removed by rotary evaporation and the product purified by two recrystallizations from methylene chloride/hexanes. ^{1}H NMR (benzene-d_6): δ 2.44−2.51 (m, 2H), 2.69−2.76 (m, 2H), 3.20−3.33 (m, 4H), 7.31 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H). MS: *m/e* 256 ($M^{\bullet+}$, 9.8%), 208 (23.1%), 134 (66.5%), 86 (55.3%), 56 (100%).

4-Morpholinyl *p*-Nitrophenyl Sulfone ($10SO_2$). MS: *m/e* 272 ($M^{\bullet+}$, 14.1%), 229 (32.5%), 186 (19.7%), 122 (23.5%), 86 (100%), 56 (69.4%).

General Photolysis Conditions. All photooxidations were carried out either in 4 mm NMR tubes or in 5 mm i.d. × 40 mm glass tubes at room temperature with continuous oxygen bubbling with the exception of those photolyses that were conducted in tubes sealed with a septum. The irradiation source was either a 500 W tungsten−halogen lamp or when a merry-go-round apparatus was used a 400 W medium pressure Hanovia lamp. The reaction mixtures were presaturated with oxygen by bubbling for 5 min prior to the irradiation. In those cases in which continuous agitation by oxygen was not possible (e.g., in sealed tubes), presaturation was done by bubbling oxygen through the reaction mixtures for 18 min. When Rose Bengal and TPP were the sensitizers, a 1 cm filter solution consisting of 0.5% $K_2Cr_2O_7$ or 12 M $NaNO_2$ was used, respectively.

Sulfide Trapping. Five different concentrations of diphenyl sulfide (0.02, 0.05, 0.1, 0.15, and 0.2 M) were used as the trapping agent with benzene solutions 0.1 and 0.2 M in **2**, and 5 × 10^{-5} M in TPP. Each reaction mixture also contained biphenyl as the internal standard and 0.13 M pyridine in order to retard bleaching of the sensitizer. The irradiations were conducted at room temperature on a merry-go-round with a 400 W medium pressure Hanovia lamp through the appropriate filter solution. Aliquots (10 μL) were removed at 20, 100, 200, and 300 s and analyzed by HPLC on a Hewlett Packard ODS Hypersil, 5 μm, 100 × 2.1 mm microbore column using 1:1 water/acetonitrile as the mobile phase and a diode array as the detector. The [**2SO**]/[Ph_2SO] ratios were determined from plots of [**2SO**] versus [Ph_2SO] using data only from those aliquots where the percent conversion of **2** was kept under 15%. Ph_2SO, **1**, **1SO**, biphenyl, and Ph_2S have retentions times of 0.76, 1.41, 0.52, 2.67, and 3.58 min, respectively, when the flow rate of the mobile phase was held at 0.6 mL/min for 1 min and then changed to 1.1 mL/min for the remainder of the analysis time.

Sulfoxide Trapping. Five different concentrations of diphenyl sulfoxide (0.02, 0.03, 0.04 or 0.05, 0.07, and 0.1 M) were used as the trapping agent with benzene and methanol solutions 0.1 and 0.2 M in **2** and 5 × 10^{-5} M in TPP and Rose Bengal, respectively. The irradiations were conducted in oxygen-saturated solutions with a 500 W tungsten−halogen lamp through the appropriate filter solution. The product concentrations, [**2SO**] and [Ph_2SO_2], were monitored relative to that of triphenylmethane by capillary GC using a Perkin-Elmer 25 m × 0.53 mm column coated with a 1 μm methyl silicone film. The [**2SO**]/[Ph_2SO_2] ratios were determined from plots of [**2SO**] versus [Ph_2SO_2] using data from only those aliquots where the percent conversion of **2** was kept under 15%. Ph_2SO_2 had a retention time of 18.0, **2SO** a retention time of 19.3, and triphenylmethane a retention time of 26.29 min when the following GC program and conditions were used: initial temperature 150 °C (13 min)−ramp (10 °C/min)−155 °C (20 min)−ramp (20 °C/min)−230 °C, detector temperature 250 °C, injector temperature 250 °C, and helium flow rate 7 mL/min.

Hammett Studies. Benzene solutions 0.05 M in **2**, 0.05 M in either a diarylsulfide or sulfoxide, 0.01 M in biphenyl, 0.13 M in pyridine, and 5 × 10^{-5} M in TPP were saturated with oxygen for 18 min and then sealed with a septum. These samples were then placed on a merry-go-round and irradiated though the appropriate filter solution with a 400 W medium pressure Hanovia lamp. Aliquots were removed at irradiation times chosen to insure less than 10% conversions of either the diaryl sulfides or diaryl sulfoxides and less than 15% conversions of **2**. Under these carefully controlled conditions it can be shown that plots of [$pXPh_2SO$] or [$pXPh_2SO_2$] versus [**1SO**] give slopes equal to $k_{PhS}[pXPh_2S]/k_S$ and $k_{SO}[pXPh_2SO]/2k_X$, respectively. These slopes divided by the slope of the line when X = H give the ratios k^X_{PhS}/k^H_{PhS} and k^X_{SO}/k^H_{SO} which are plotted versus σ_p^+ and σ_p°,[31] respectively.

***k*$_T$ Measurements.** The k_T values were obtained in benzene using the apparatus and procedure previously described.[32] Sulfenamide concentrations were chosen in order to observe decreases in lifetime of singlet oxygen over a range of approximately 25−15 μs. The k_T values were obtained from the experimental lifetimes by plotting k_{obsd} versus the concentration of sulfenamide used for the particular experiment. Each k_T value was determined at least twice with a precision of ±15%.

***k*$_r$ Measurements.** The k_r measurements were done in benzene using the procedure of Foote and Higgins.[22] The competitive photooxidations of **2** were carried out versus adamantylideneadamantane and $\Delta^{9,10}$-octalin. The competitive photooxidations of **9** were carried out versus α-pinene.

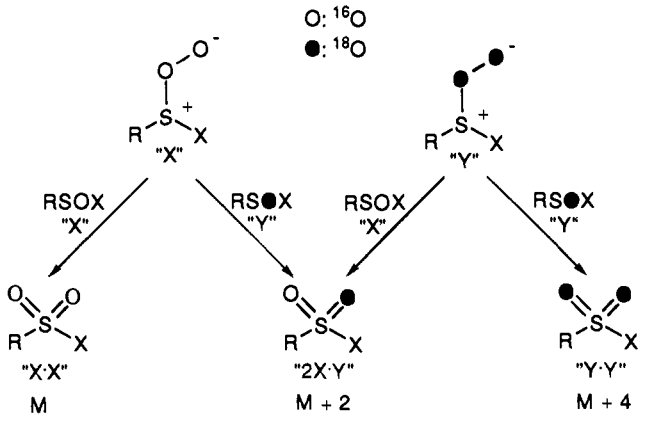
Isotopic Labeling Studies. Benzene solutions 0.05 M in substrate, 0.13 M in pyridine, and 5 × 10^{-5} M in TPP were placed in reaction vessels saturated with nitrogen and subjected to five freeze−pump−thaw cycles before final introduction of the isotopic gas mixture. The samples were irradiated on a merry-go-round through a 1 cm path length of a 12 M $NaNO_2$ filter solution. Aliquots were removed at various times and analyzed immediately by GC/MS. The presence of the pyridine prevented dye bleaching without any detrimental effect on the photooxidations.

The experimental $(M)/(M+2)/(M+4)$ ratio was adjusted by correcting the $M+2$ and $M+4$ peaks for $M+2$ contributions from the molecular ion. The $M+2$ contribution to the molecular ion was

(31) Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: Essex, England, 1987; pp 828.

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

Scheme 4



determined by measuring the $(M + 2)/M$ ratio in the parent sulfenamide (this value differs from the $M + 2$ contribution from the sulfonamide molecular ion by $2 \times 0.2\%$, the contribution from the ^{18}O isotope). The corrected $M + 2$ sulfonamide is then given by $(M + 2)_{corrected} = (M + 2)_{sulfonamide} - [(M)_{sulfonamide} \times [(M + 2)/M]_{sulfenamide}]$ and the $(M + 4)_{corrected} = (M + 4)_{sulfonamide} - [(M + 2)_{corrected} \times [(M + 2)/M]_{sulfenamide}]$. In those cases where a correction from the $M + 4$ peak of the molecular ion was necessary it was done in the same way as described above. The data treated in this way result in a $[(M)/(M + 2)/(M + 4)]_{corrected}$ which reflects only contributions from the oxygen isotopes.

The theoretical $(M)/(M + 2)/(M + 4)$ ratio for the bimolecular mechanism was calculated as depicted in Scheme 4. The probability for formation of a $^{32}O_2$-persulfinyl intermediate and a $^{36}O_2$-persulfinyl intermediate is X and Y, respectively. The ratio X/Y depends on the configuration of the isotopically enriched oxygen gas. The ratio of the probability for the formation of ^{16}O-sulfinyl and ^{18}O-sulfinyl products is also X/Y. In the bimolecular pathway persulfinyl intermediates are trapped by the sulfinyl products. Thus the probability for the formation of a sulfonyl product is $X \cdot X = X^2$, if it is formed through the trapping of a $^{32}O_2$-persulfinyl intermediate by a ^{16}O-sulfinyl product, or $Y \cdot Y = Y^2$, if it is formed via the trapping of a $^{36}O_2$-persulfinyl intermediate by a ^{18}O-sulfinyl product. In both these cases, the two oxygen atoms in the sulfonyl product are the same isotope. There are two routes for the formation of a sulfonyl product in which the two oxygen atoms are different isotopes (i.e., through the trapping of a $^{32}O_2$-persulfinyl intermediate by a ^{18}O-sulfinyl product or the trapping of a $^{36}O_2$-persulfinyl intermediate by a ^{16}O-sulfinyl product). Thus the probability for the formation of a $^{16}O-^{18}O$ labeled sulfonyl product is $2XY$. Overall, the theoretical $(M)/(M + 2)/(M + 4)$ ratio for the bimolecular mechanism is $X^2/2XY/Y^2$. Since the X/Y ratio in the oxygen gas used is 1.324/1, the $(M)/(M + 2)/(M + 4)$ ratio is $(1.324)^2/(2 \times 1.324)/1^2 = 1.753/2.648/1$. The theoretical $(M)/(M + 2)/(M + 4)$ ratio for the unimolecular mechanism is just $X/0/Y = 1.324/0/1$ since the oxygen gas is devoid of $^{34}O_2$.

The contribution to the $M + 2$ peak by the two mechanisms is $2XYf_{BM} + 0f_{UM}$, where f_{BM} is the fraction of the reaction that goes by the bimolecular mechanism and f_{UM} is the fraction that goes via the unimolecular mechanism. The contribution to the $M + 4$ peak by the two mechanisms is $Y^2f_{BM} + Yf_{UM}$. The ratio of the $M + 2$ to $M + 4$ peak is therefore given by the following equation:

$$\frac{M+2}{M+4} = \frac{2XYf_{BM} + 0f_{UM}}{Y^2f_{BM} + Yf_{UM}} = \frac{2XYf_{BM}}{Y^2f_{BM} + Yf_{UM}}$$

Which can be solved for f_{BM} since $Y = 1$ and $f_{BM} + f_{UM} = 1$.

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