

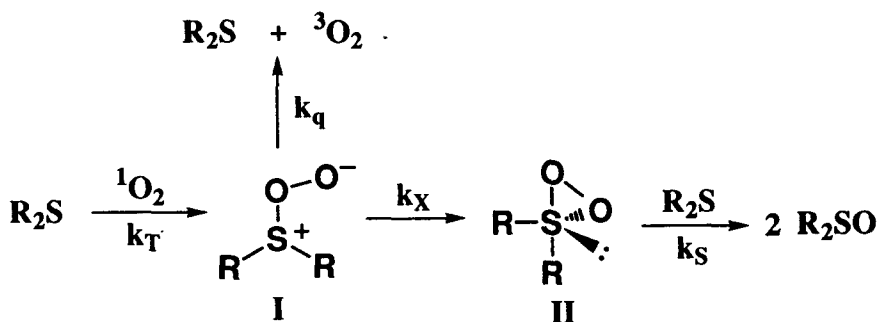
Steric and Electronic Effects on the Partitioning of a Persulfinyl Intermediate Along the Physical Quenching and Chemical Reaction Channels.

Edward L. Clennan,* Alexander Greer

Department of Chemistry
 University of Wyoming
 Laramie WY 82071

Abstract: The rate constants, k_T , k_r , and k_Q , corresponding to the substrate induced total removal, chemical removal, and physical removal of singlet oxygen, respectively, have been measured for a series of sulfenamides. The structural effects on the partitioning of the persulfinamide intermediate along the chemical and physical deactivation pathways is discussed. Copyright © 1996 Elsevier Science Ltd

Footo and coworkers pointed out more than 25 years ago that sulfides remove singlet oxygen from solution at a significantly faster rate, k_T , than products are produced, k_r .¹ Furthermore, the quantum yield for the formation of diethylsulfoxide, which could theoretically be as large as 2, is in fact less than 0.05. (Scheme 1) Footo and coworkers demonstrated that it was the decomposition of a persulfoxide intermediate, I in Scheme 1, to sulfide and triplet oxygen in a physical quenching process, k_Q , which was responsible for the reaction inefficiency.²



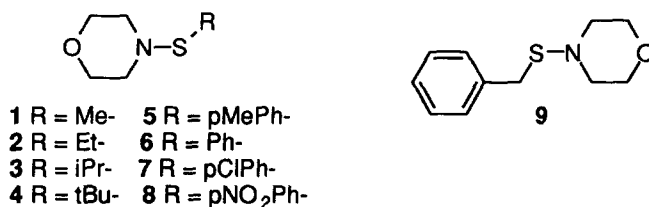
Scheme 1

With the advent of a technique to directly monitor the disappearance of ${}^1\text{O}_2$ the values of k_T , the rate constants for substrate induced removal of ${}^1\text{O}_2$ are now available with a high degree of accuracy.³ The rate constants for product formation, k_r , are also available, often via a competition technique, with a reasonable degree of accuracy. Consequently, the remaining bimolecular rate constant of interest, k_Q , can be obtained by

difference using equation 1. The variable α in equation 1 is a function of the product composition. When sulfoxide is the exclusive product $\alpha = 0.5$ since for each molecule of singlet oxygen that disappears two molecules of product are formed. On the other hand, when sulfone is the exclusive product $\alpha = 1.0$. Unfortunately, as pointed out above, k_f for sulfides is very small in comparison to k_T and the difference ($k_Q = k_T - \alpha k_f$) cannot be determined accurately.

$$k_T = \alpha k_f + k_Q \quad 1$$

A different situation is encountered during the photooxidations of sulfenamides, **1** - **8**.^{5,6} (Eqn. 2) These reactions are considerably more efficient than sulfide photooxidations and as a result k_T and k_f are of the same order of magnitude. In addition, detailed kinetic studies with 4-morpholinyl benzyl sulfide, **9**, have demonstrated that the reaction surface describing the interaction of singlet oxygen with sulfenamides is topographically similar to the Foote reaction surface for diethylsulfide (Scheme 1). Consequently, these substrates provide the first opportunity to accurately measure the steric and electronic effects on the k_x/k_q (Scheme 1) ratio.



The rate constants k_T were determined in oxygen saturated benzene by monitoring the ability of **1-8** to quench the phosphorescence of ¹O₂ at 1270 nm using the laser based emission apparatus previously described.^{7,8} The rate constants for product formation, k_f , were determined by competition with $\Delta 9(10)$ -octalin and cyclohexene for sulfenamides **1-7** and **8**, respectively, using the method of Higgins and Foote.⁹ The rate constants for physical quenching, k_Q , were determined using equation 1. The observed rate constants, k_f and k_Q , are related to the microscopic rate constants depicted in Scheme 1 as shown in equations 2 and 3. These equations were derived from steady state treatment of both intermediates **I** and **II** in Scheme 1 and demonstrate that 1/2 of the k_f/k_Q ratio is equal the microscopic rate constant ratio k_x/k_q . This ratio, k_T , k_f , k_Q , and the % of the persulfenamide intermediate (**I** in Scheme 1) which partitions along the chemical reaction channel are given in Table 1 for photooxidations of sulfenamides **1-8**.

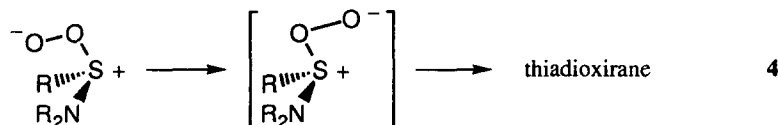
$$k_r = 2k_T \left(\frac{k_X}{k_X + k_q} \right) \quad 2 \quad k_Q = k_T \left(\frac{k_q}{k_X + k_q} \right) \quad 3$$

Table 1. Kinetic Data for the Photooxidations of Sulfenamides 1-8.

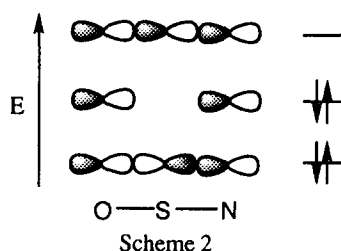
Compound	$k_T(\text{M}^{-1}\text{s}^{-1})$	$k_r(\text{M}^{-1}\text{s}^{-1})$	$k_Q(\text{M}^{-1}\text{s}^{-1})$	k_x/k_q	% k_x
1 (R = Me-)	$1.46 \pm 0.12 \times 10^7$	$7.59 \pm 0.04 \times 10^6$	1.06×10^7	0.358	26 ± 2
2 (R = Et-)	$8.85 \pm 0.57 \times 10^6$	$4.63 \pm 0.16 \times 10^6$	6.44×10^6	0.360	26 ± 2
3 (R = iPr-)	$3.51 \pm 0.02 \times 10^6$	$2.06 \pm 0.07 \times 10^6$	2.36×10^6	0.436	30 ± 2
4 (R = tBu-)	$7.13 \pm 0.78 \times 10^4$	$4.34 \pm 0.69 \times 10^4$	4.87×10^4	0.446	31 ± 2
5 (R = pMePh-)	2.61×10^5	$1.40 \pm 0.15 \times 10^5$	1.88×10^5	0.372	27 ± 2
6 (R = Ph-)	2.32×10^5	$8.04 \pm 0.39 \times 10^4$	1.89×10^5	0.213	18 ± 2
7 (R = pClPh-)	1.13×10^5	$3.61 \pm 0.49 \times 10^4$	9.35×10^4	0.193	16 ± 2
8 (R = pNO ₂ Ph-)	2.39×10^4	$5.82 \pm 0.78 \times 10^3$	2.01×10^4	0.145	13 ± 2

The initial interaction of $^1\text{O}_2$ at sulfur as measured by k_T is significantly more sensitive to steric than to electronic effects as revealed by a $[(k_T)_{\text{fastest}}/(k_T)_{\text{slowest}}]$ of 205 for the alkyl substituted sulfenamides 1-4 but of only 11 for the aryl substituted sulfenamides 5-8. The importance of steric interactions in 1-4 is corroborated by the observation of an excellent linear correlation in a Taft plot when $\log(k_T^R/k_T^{\text{Me}})$ is plotted versus E_s ($\delta = 1.47$; $r = 0.997$).¹⁰ The importance of electronic interactions in 5-8 is likewise corroborated by a Hammett plot of $\log(k_T^{\text{pX}}/k_T^{\text{H}})$ versus σ to give a reaction constant ρ of -1.15 ($r = 0.992$).

The partitioning between the physical quenching and chemical reaction channels, however, shows only a slight sensitivity to steric effects in dramatic contrast to the large effect on k_T . The small increased preference for the chemical reaction channel as the size of the substituent R is increased in compounds 1-4 might reflect a greater relief of steric strain in the rotation¹¹ accompanying collapse to the thiadioxirane than in the S-O bond elongation on the very exothermic physical quenching surface. (Eqn. 4)



Electronic effects, on the other hand, play a substantial role in determining the overall outcome of the reaction. As the substituent on the sulfenamide is changed from pMePh- to pNO₂Ph- the percent of persulfenamide which is converted to product decreases from 27 to 13%. (% k_x in Table 1) Clearly the substituent effects demand that the amount of positive charge on sulfur that disappears is greater in the transition state for physical quenching than in the transition state for conversion to the thiadioxirane. This is consistent with the molecular orbital picture of sulfuranes (Scheme 2) which places excess electron density on the terminal atoms of the 4-electron 3-centered bond and a deficiency of electron density on sulfur.¹²



Acknowledgment: We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

References

1. Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795-3796.
2. Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717-4721.
3. Krasnovski, A. A. *Photochem. Photobiol.* **1979**, *29*, 29-36.
4. The % sulfoxide and corresponding α values are; 1 94%(0.53); 2 97%(0.52); 3 88%(0.56); 4 96%(0.52); 5 96%(0.52); 6 95%(0.53); 7 93%(0.54); 8 70%(0.65). $\alpha = 0.5(\text{fraction sulfoxide}) + \text{fraction sulfone}$. The fraction of sulfoxide is the average value observed in the k_t determination.
5. Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809-810.
6. Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218-4227.
7. Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581-3584.
8. Clennan, E. L.; Noe, L. J.; Szneler, E.; Wen, T. *J. Am. Chem. Soc.* **1990**, *112*, 5080-5085.
9. Higgins, R.; Foote, C. S.; Cheng, H. In *Advances in Chemistry Series*; R. F. Gould, Ed.; American Chemical Society: Washington D. C., 1968; Vol. 77; pp 102-117.
10. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, N. Y., 1987.
11. The ab initio preferred geometry of both persulfoxide and persulfenamide is one in which the O-O bond bisects or nearly bisects the C-S-X bond. Greer, A.; Jensen, F.; Clennan, E. L. unpublished results.
12. Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; F. Bernardi, I. G. Csizmadia and A. Mangini, Ed.; Elsevier: Amsterdam, The Netherlands, 1985; Vol. 19; pp 408-483.

(Received in USA 29 May 1996; revised 25 June 1996; accepted 27 June 1996)