Photooxidation of Alkyl 4-Nitrophenyl Sulfides and Sulfoxides. Observation of Oxidative C–S Bond Cleavage and Rearrangement Reactions

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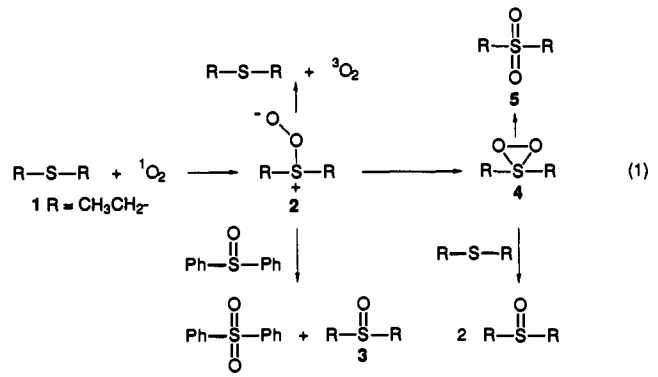
Abstract: Alkyl 4-nitrophenyl sulfides and sulfoxides undergo a self-photoinduced, singlet oxygen oxidation to produce a variety of products, including sulfonates and carbonyl compounds formed by the oxidative cleavage of the C–S bond of the sulfides and sulfoxides. Structural rearrangements are observed in the resulting carbonyl compounds formed in the oxidative cleavage of the C–S bond in the *tert*-amyl and 2-phenylethyl sulfides. An overall mechanism is proposed which involves the formation of peroxysulfoxides and peroxysulfones which undergo heterolytic C–S bond cleavage to form ion pairs which recombine to form persulfenates or persulfinates which then undergo photo- and/or thermally-induced homolytic O–O bond cleavage to form alkoxy and sulfinyl or sulfonyl radicals. The alkoxy radicals undergo β-scission, disproportionation, or recombination with the sulfonyl radical to form the observed products. These C–S oxidative cleavage reactions have only been rarely observed in the earlier studies on the singlet oxygen oxidation studies of dialkyl sulfides, and are attributed, in part, to the presence of the 4-nitro group on the aromatic ring which greatly affects the susceptibility of the sulfur atom of the sulfides and sulfoxides toward nucleophilic attack, and on the reactivity of the peroxysulfoxides and peroxysulfones toward heterolytic cleavage of the O–S bond.

Introduction

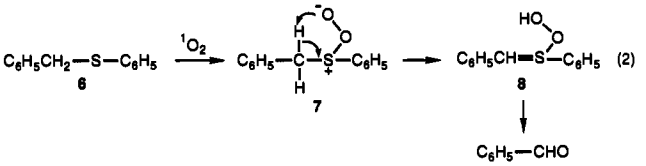
The reactions of dialkyl (**1**), alkyl phenyl, and diaryl sulfides with singlet oxygen ($^1O_2$), generated by the photosensitized conversion of triplet oxygen to $^1O_2$, have been extensively studied.[1] The reaction of dialkyl sulfides with $^1O_2$ was first reported by Schenck and Krauch in 1962.[2] In the intervening decades, the results of extensive studies by Foote and co-workers[3] have led to the suggestion that two intermediates are involved in the $^1O_2$ oxidation of diethyl sulfide to the corresponding sulfoxide **3** and sulfone **5**; one being a nucleophilic "peroxysulfoxide" (**2**) which is stabilized in protic solvents by hydrogen bonding, the other being an electrophilic "thiadioxirane" (**4**) which is formed in nonprotic solvents (eq 1).[3a] The intermediate peroxysulfoxide



(1)

reacts with diphenyl sulfoxide (electrophilic) to produce diphenyl sulfone and diethyl sulfoxide, while the thiadioxirane intermediate can react with starting sulfide (nucleophilic) to produce two molecules of diethyl sulfoxide (**3**) or undergo ring opening to form diethyl sulfone (**5**). The intermediacy of the thiadioxirane in the $^1O_2$ oxidation of a sulfide to form sulfone is supported by the results of oxygen labeling studies in which reaction with a mixture of $^{16}O_2$ and $^{18}O_2$ results in the predominant formation of non- and doubly-labeled sulfone.[4] The results of a very recent theoretical study have provided support for the existence of both the peroxysulfoxide and thiadioxirane intermediates as minimum-energy structures on the hypersurfaces for the reaction of H_2S and $(CH_3)_2S$ with $^1O_2$, with predicted energy barriers for the formation and reactions of the intermediates and products in the oxidation process.[5]

In the reaction of certain sulfides, oxidative cleavage of the C–S bond has been observed. Corey and Ouannès have reported that the reaction of benzyl phenyl sulfide (**6**) with $^1O_2$ results in the formation of benzaldehyde.[6] No other organic products derived from the benzyl group were reported. The benzaldehyde was proposed to be formed via the mechanism shown in eq 2,in



(2)

which an intramolecular proton transfer occurs within the peroxysulfoxide **7** to produce the intermediate **8**, which undergoes further unspecified reaction to form benzaldehyde.[6] A similar mechanism has been proposed for the hydroxylation of thiazolidine

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(1) For a recent comprehensive review of the reactions of $^1O_2$, see: Gorman, A. A. The Bimolecular Reactivity of Singlet Molecular Oxygen. In *Advances in Photochemistry*; Volman, D., Hammond, G., Neckers, D, Eds.; John Wiley and Sons: New York, 1992; pp 218–274.

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

(3) (a) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, *114*, 3015. (b) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478–1485. (c) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717. (d) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949. (e) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765–769. (f) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

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

(5) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478–6487.

(6) Corey, E. J.; Ouannès, C. *Tetrahedron Lett.* **1976**, 4263–4267 (No. 47).

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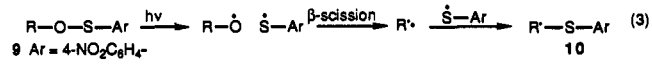
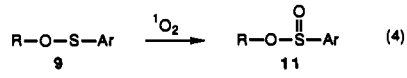
derivatives α to the sulfur atom,[7] and Foote and co-workers have observed the oxidative cleavage of the C–S bonds in substituted thiiranes[3b] and in 1,5-dithiacyclooctane during reaction with $^1O_2$.[3a]

Recent studies in the authors' laboratories on the photoinduced, homolytic dissociation of alkyl 4-nitrobenzenesulfenates **9** to form the sulfides **10** (eq 3)[8] in the presence of oxygen resulted in the





discovery of a unique, self-photoinduced oxidation of the sulfenates **9** to the corresponding sulfinates **11** (eq 4).[9] (No added sensitizer is required in these oxidation reactions.) The results of theoretical studies indicated that the lowest-energy electronic transition of the alkyl 4-nitrobenzenesulfenates ($\lambda_{max} \sim 347$ nm) involves the excitation of a 3pπ, nonbonded-pair electron on the sulfur atom (the HOMO).[9] The oxidation of the sulfenates is quenched by the presence of *trans*-1,3-pentadiene, suggesting that the triplet excited state of the 4-nitrobenzenesulfenate results in the conversion of $^3O_2$ to $^1O_2$.[9] The presence of 1,3-cyclohexadiene also quenches the oxidation of the sulfenates and results in the formation of the corresponding endoperoxide of 1,3-cyclohexadiene, indicating the formation of $^1O_2$, the oxidation of the sulfenate resuming after complete consumption of the 1,3-cyclohexadiene.[9]

Along with the $^1O_2$ oxidation of the alkyl 4-nitrobenzenesulfenates to the corresponding sulfinates (eq 3), unexpected oxidation products were also formed, the formation of which could only be rationalized as being derived from the oxidation of the alkyl 4-nitrophenyl sulfides formed competitively via eq 3.[10] Those observations have led to a detailed investigation of the self-photoinduced $^1O_2$ oxidation of a variety of alkyl 4-nitrophenyl sulfides and sulfoxides. The results of these studies have led to the suggestion that peroxysulfoxides and peroxysulfones are formed which are capable of undergoing heterolytic fragmentation of the C–S bond to form ion pairs which recombine to form persulfenates and persulfinates. Rearrangement in the carbocation of the ion pairs results in the ultimate formation of rearranged products. Photo- or thermally-induced O–O bond homolysis of the persulfenates or persulfinates produces alkoxy radicals which can either undergo β-scission, disproportionation, hydrogen atom transfer to a sulfur-centered radical, or combination with a sulfinyl or sulfonyl radical.

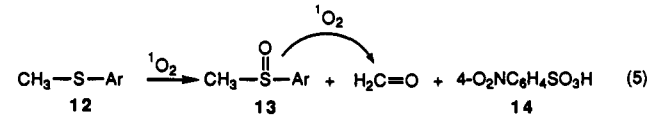
Results

General Comments. The alkyl 4-nitrophenyl sulfides possess λ_{max}'s at $\sim$345 nm and are thus potentially capable of sensitizing the conversion of $^3O_2$ to $^1O_2$. No added sensitizer is required in the photooxidation reactions of the alkyl 4-nitrophenyl sulfides described in this article.[11] The alkyl 4-nitrophenyl sulfoxides possess λ_{max}'s at $\sim$300 nm with tailing end absorption to >350 nm. Again, no added sensitizer is required for the photooxidation of the 4-nitrophenyl sulfoxides. The self-photoinduced oxidations of the alkyl 4-nitrophenyl sulfides and sulfoxides described in this article have been carried out in $CDCl_3$ solution under an oxygen atmosphere at 350-nm-wavelength light. All products have been identified by comparison of their ^1H NMR spectral characteristics with those of authentic substances.

Table 1. Relative Yields of Products Formed and Rates in the Self-Photoinduced $^1O_2$ Oxidation of Sulfoxides 17a–c

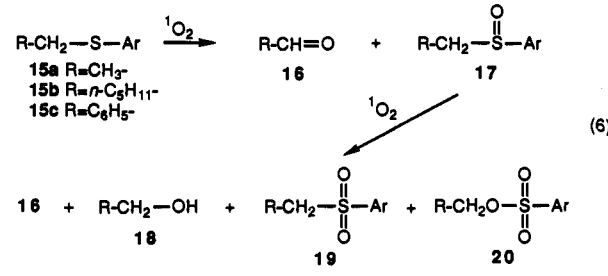
sulfoxide	16	18	19	20	reaction time
17a	13	5	51	32	2 days
17b	28	trace	42	30	2 days
17c	49		20	31	1 day

Specific Systems. The self-photoinduced oxidation of methyl 4-nitrophenyl sulfide (**12**) produces only the corresponding sulfoxide **13** (eq 5). Methyl 4-nitrophenyl sulfone and methyl



4-nitrobenzenesulfonate are *not* formed. The continued irradiation of **13** resulted in the rather slow disappearance of **13** with the formation of 4-nitrobenzenesulfonic acid (**14**) as the only detectable product.[12] No characterizable product(s) derived from the methyl group is (are) detected by ^1H NMR analysis of the reaction solution.[12]

The photooxidation of the ethyl sulfide **15a** results in the formation of acetaldehyde (**16a**, 65%), ethanol (**18a**, 2%), sulfoxide **17a**, sulfone **19a**, and sulfonate **20a** (eq 6). The yield



of the sulfoxide **17a** increases with time to a maximum yield of $\sim$40% and then decreases with continued formation of sulfone **19a** and sulfonate **20a**. Starting with pure sulfoxide **17a** results in the formation of acetaldehyde (in considerably lower yields than directly from sulfide **15a**), ethanol, sulfone **19a**, and sulfonate **20a**. The final relative yields and time for the complete disappearance of the sulfoxide **17a** are given in Table 1.

The photooxidation of 1-hexyl 4-nitrophenyl sulfide (**15b**) gives similar results, producing hexanal (**16b**, 73%) and the sulfoxide **17b**, which reaches a maximum yield of $\sim$37% and then decreases with continued formation of sulfone **19b** and sulfonate **20b**. The photooxidation of the pure sulfoxide **17b** results in the formation of aldehyde **16b** (again in significantly lower yield than derived directly from the sulfide **15b**), sulfone **19a**, and sulfonate **20a**. The final relative yields are given in Table 1.

The photooxidation of the benzyl sulfide **15c** occurs considerably faster than does the oxidation of **15a** or **15b** and produces benzaldehyde (**16c**, 76%) along with small quantities of benzyl alcohol (**18c**) and sulfonate **20c**. Sulfoxide **17c** was not detected

(7) Takate, T.; Hoshino, K.; Takeuchi, E.; Tamura, Y.; Ando, W. *Tetrahedron Lett.* **1984**, *25*, 4767–4770. Takata, T.; Tamura, Y.; Ando, W. *Tetrahedron* **1985**, *41*, 2133–2137.

(8) Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990**, *55*, 5815–5816.

(9) Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *55*, 5815–5816.

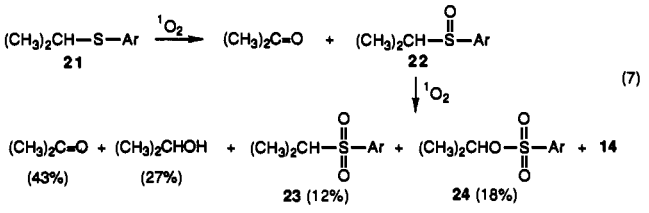
(10) Pasto, D. J.; Cottard, F. *J. Am. Chem. Soc.* **1994**, *116*, in press.

(11) Methylene blue sensitization and $^1O_2$ trapping experiments have been attempted. Irradiation of 2-phenylethyl 4-nitrophenyl sulfides in the presence of $\sim 10^{-5}$ methylene blue in $CDCl_3$ with >400-nm-wavelength light results in the oxidation of the sulfide. However, the color of the methylene blue disappears quite quickly. Further addition of methylene blue results in similar behavior. The photooxidation of methyl 4-nitrophenyl sulfide in the presence of a 250% molar excess of 1,3-cyclohexadiene is quenched along with formation of the endo peroxide of 1,3-cyclohexadiene. However, continued irradiation results in the destruction of the endo peroxide. It must be concluded that some reactive intermediate formed in the photooxidation of the sulfide (probably the proposed alkoxy radicals) reacts with the methylene blue and the endo peroxide, resulting in their destruction.

(12) Formaldehyde, which is believed to be the oxidation product, is of such volatility that it could not be retained in solution, and its polymer paraformaldehyde is not soluble in $CDCl_3$, which is used as the solvent for the photooxidation reactions.

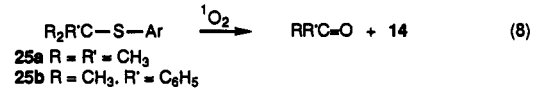
as an intermediate during the course of the oxidation of **15c**. The photooxidation of pure sulfoxide **17c** produces benzaldehyde (again in significantly lower yield than directly from the sulfide **15c**), sulfone **19c**, and sulfonate **20c**. The final relative yields are given in Table 1. The photooxidation of sulfoxide **17c** also occurs significantly faster than does the oxidation of sulfoxides **17a,b**.

The photooxidation of isopropyl 4-nitrophenyl sulfide (**21**) produces acetone as the major product derived from the isopropyl group. Only trace quantities of sulfoxide are detected during the course of the reaction, and no corresponding sulfone or sulfonate is detected. The photooxidation of the pure sulfoxide **22** results in the formation of acetone along with substantial quantities of sulfone **23**, sulfonate **24**, and 2-propanol (the relative yields are given in eq 7). The H–D isotope effect for the photooxidation of **21** has been determined by monitoring the relative rate of disappearance of **21** versus 2-deuterio-**21**, giving a value of k_H/k_D of 1.92 ± 0.2.



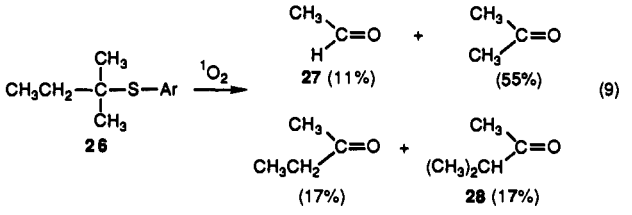
(7)

tert-Butyl 4-nitrophenyl sulfide (**25a**) and 2-phenyl-2-propyl 4-nitrophenyl sulfide (**25b**) undergo photooxidation to produce essentially quantitative yields of acetone and acetophenone (eq 8). No sulfone or sulfonate is detected during the course of the photooxidation reactions.



(8)

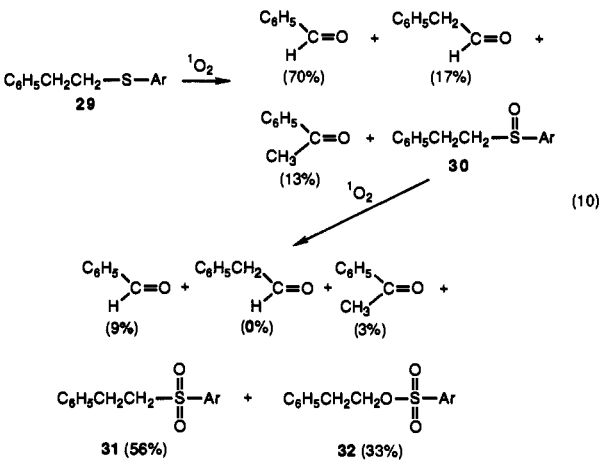
The photooxidation of the *tert*-pentyl sulfide **26** results in an essentially quantitative yield of the carbonyl-containing products shown in eq 9, including the structurally rearranged aldehyde **27** and ketone **28**. No sulfoxide, sulfone, or sulfonate formation is detected during the course of the photooxidation reactions.



(9)

The photooxidation of the 2-phenylethyl sulfide **29** results in the formation of the carbonyl-containing products shown in eq 10 (including the structurally rearranged products benzaldehyde and acetophenone), sulfoxide **30** (which reaches a maximum yield of ~35% during the course of the reaction), sulfone **31**, and sulfonate **32**. The photooxidation of sulfoxide **30** produces the carbonyl-containing compounds in significantly lower and different yields than observed in the photooxidation of the sulfide **29**, with dominant formation of sulfone **31** and sulfonate **32**. The relative yields of the carbonyl-containing products derived from the photooxidation of the sulfide **29** and sulfoxide **30** are given under the structures in eq 10. It is important to note the difference in the relative yields of the carbonyl-containing products derived directly from the sulfide **29** and from the sulfoxide **30**.

Although is was not feasible to quantitatively measure the rates of disappearance of the sulfides or sulfoxides, the qualitative trend in relative reactivities of the sulfoxides is methyl (5–7 days)



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≪ pri-alkyl (2 days) < benzyl (1 day) ~ isopropyl (~15 h) < *tert*-alkyl (5 h).

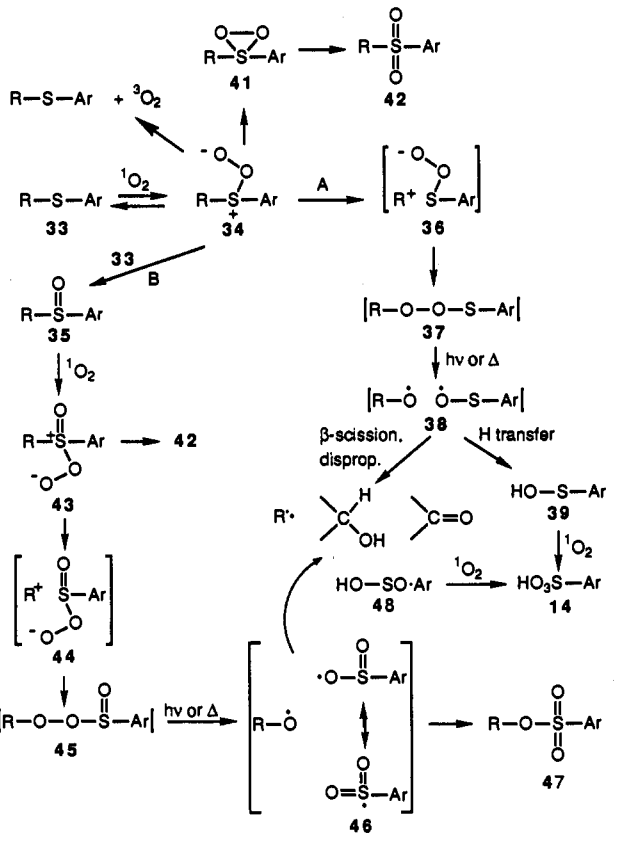
Discussion

The basic data leading to the proposed mechanism for the photooxidation of the alkyl 4-nitrophenyl sulfides and sulfoxides are the observations of (1) the formation of the structurally rearranged carbonyl compounds **26** and **29**; (2) the relative reactivity for the formation of the oxidative C–S bond cleavage products; (3) the degree of sulfone and sulfonate formation as a function of the degree of substitution at the alkyl carbon atom bonded to the sulfur atom in the sulfides and sulfoxides; (4) the formation of carbonyl products formed by the loss of a hydrogen atom or an alkyl group; and (5) in a more subtle sense the H–D kinetic isotope effect observed in the oxidation of isopropyl 4-nitrophenyl sulfide. The rearrangement reactions can only have occurred in carbocation intermediates, and the carbonyl compounds can only be formed by a hydrogen atom transfer or by the β-scission of an alkoxy radical.

The results described in the foregoing paragraphs cannot be rationalized on the basis of the mechanism shown in eq 2. The relative reactivity sequence of methyl < ethyl < isopropyl is *not* consistent with an intramolecular proton transfer, the relative acidity in the sequence decreasing and making such a proton transfer increasingly more difficult. In addition, the mechanism shown in eq 2 cannot explain the formation of the carbonyl-containing products formed in the oxidation of the *tert*-alkyl 4-nitrophenyl sulfides **25a**, **25b**, and **26** or the rearranged products formed from **26** and **29**.

The observed results can best be rationalized in terms of the overall mechanism shown in Scheme 1, which incorporates some steps similar to those proposed earlier for the $^1O_2$ oxidation of dialkyl sulfides.[3] In a preoxidation sequence of steps (not shown), the alkyl aryl sulfide **33** undergoes electronic excitation (λ_{max}s ~ 345 nm) to initially produce the singlet excited state which undergoes intersystem crossing to produce the triplet excited state (experimentally demonstrated in the oxidation of the alkyl 4-nitrobenzenesulfenates[9] and implied by the data described in footnote 11). The triplet excited state than sensitizes the conversion of $^3O_2$ to $^1O_2$. The $^1O_2$ thus formed then reacts with ground-state **33** to produce the peroxysulfoxide **34**. The peroxysulfoxide **34** is proposed to be formed reversibly, resulting in "physical quenching" of the $^1O_2$, or to lead to the formation of products via pathway A or B shown in Scheme 1. When the alkyl group of the sulfide is not sterically demanding and is not capable of forming a reasonably stable carbocation, **34** reacts with another molecule of sulfide **33** to produce the sulfoxide **35**. This is in contrast with the diethyl sulfide system studied by Foote and co-workers[3] in which the proposed peroxysulfoxide does not react with the nucleophilic diethyl sulfide. In the present system, however, the 4-nitro group of the aryl system must impart some

Scheme 1



electrophilic character to the sulfur atom (via resonance donation of the sulfur nonbonded pair of electrons into the 4-nitrophenyl π system), making it prone toward nucleophilic attack and oxidation by the peroxysulfoxide intermediate. When the alkyl group is more sterically demanding and the alkyl group can form a reasonably stable carbocation, heterolytic fragmentation of the C–S bond to form the ion pair **36** can occur. The heterolytic fragmentation is favored by the presence of the 4-nitro group on the aromatic ring, which in the heterolytic fragmentation process the sulfur atom looses its formal positive charge and accepts a nonbonding pair of electrons which can be delocalized by interaction with the 4-nitrophenyl system. Studies on the reaction of isopropyl phenyl sulfide (lacking the 4-nitro group) with $^1O_2$ indicate that the oxidative cleavage of the C–S bond occurs much more slowly.[13] The oxidative C–S bond cleavage shown in eq 2 does not enjoy the effect of a 4-nitro group, but the stability of the benzyl cation formed will facilitate the heterolytic cleavage of the C–S bond.

The observation of a substantial k_H/k_D of 1.92 in the photooxidation of isopropyl 4-nitrophenyl sulfide (**21**) suggests that the rate-determining step in the formation of the C–S bond cleavage products is the heterolytic cleavage of the C–S bond to form the ion pair **36**. During this cleavage process the carbon atom attached to the sulfur atom undergoes a change in hybridization from sp^3 to sp^2. This change in hybridization results in an increase in the stretching force constant of the C–H (C–D) bond which is expected to result in a less than unity k_H/k_D, not greater than unity as observed. The dominant contribution to the observed k_H/k_D must arise from the loss of the H(D)–C–S bending frequency, which will give rise to a greater than unity isotope effect.[14] The qualitative observation that the rate of oxidation, to form either the sulfoxide or the C–S bond cleavage products, increases as the size and the carbocation stability of the alkyl group increases suggests that the formation of the peroxysulfoxide **34** is reversible, there being no reason to expect that the rate of formation of the peroxysulfoxide intermediate **34** should increase as the size of the alkyl group increases. In fact, the opposite should be true.

Recombination of the ion pair **36** will form the persulfenate **37** which, either photochemically or thermally,[15] can undergo homolytic cleavage of the O–O bond to form the radical pair **38**. Hydrogen atom transfer from the α-carbon atom of the alkoxy radical to the sulfinyl radical will produce the sulfenic acid **39** and a carbonyl compound. The sulfenic acid is then proposed to undergo further oxidation to produce 4-nitrobenzenesulfonic acid (**14**). With the *tert*-alkoxy radicals derived from the *tert*-alkyl sulfides (and sulfoxides), β-scission is the only reaction possible, leading to the formation of ketonic products.[16]

The structural rearrangement of the carbocation R^+ in **36** followed by recombination to form the persulfenate will produce a structurally rearranged alkyl persulfenate which will ultimately lead to the formation of the structurally rearranged carbonyl products **27** and **28** from **26** and benzaldehyde and acetophenone from **29**. In the case of **26**, the cationic rearrangement (proton migration) is contrathermodynamic but leads to a less sterically congested product, i.e., a *sec*- versus a *tert*-alkyl persulfenate derivative. In the case of **29**, the proton migration is strongly thermodynamically favored, going from a primary to a benzyl-type cation.

The oxidation of the sulfoxides is proposed to occur via the formation of the peroxysulfone intermediates **43**. Heterolytic cleavage of the peroxysulfones, again favored by the presence of the 4-nitro group and increasing stability of the carbocation, results in the formation of the ion pair **44**, in which structural rearrangement within the carbocation can occur. Recombination of the ion pair **44** will produce the persulfinate **45**. The photochemically- or thermally-induced homolytic fragmentation of the O–O bond in **45** will produce the alkoxy and sulfonyl (**46**) radical pair, the recombination of which will produce the sulfonate **47**.[17] Hydrogen atom transfer from a *sec*-alkoxy radical to the sulfonyl radical will produce a carbonyl compound and 4-nitrobenzenesulfinic acid, which then must undergo further photooxidation to produce **14**. Disproportionation of the alkoxy radical will produce the corresponding ketone and alcohol.

The relative rate of further reaction of the sulfoxide **35** with $^1O_2$ is also very sensitive to the nature of the alkyl group. Only when the alkyl group is capable of forming a reasonably stable carbocation does further oxidation occur in a facile manner. In the cases where the alkyl group is methyl or ethyl, the oxidative cleavage of the C–S bond is very slow. However, when the alkyl group is capable of forming a reasonably stable carbocation, such as isopropyl and benzyl, further photooxidation occurs more rapidly, producing sulfone **42** and sulfonate **47**. Again, the very slow further oxidation of the methyl and ethyl sulfoxide derivatives compared to the isopropyl and benzyl derivatives suggests that peroxysulfone formation is reversible.

The peroxysulfoxide **34** does not appear to undergo ring closure to form the thiadioxirane intermediate **41**, which, in addition to the formation of sulfoxide **35** by reaction with **33**, should also result in the formation of the sulfone **42** as observed in the photooxidation of diethyl sulfide.[3] Although sulfone formation

(13) Pasto, D. J.; Cottard, F. Preliminary observations.

(14) Shiner, V. J., Jr. Isotope Effects and Reaction Mechanisms. In *Isotopes and Chemical Principles*; Rock, P. A., Ed.; American Chemical Society: Washington, DC, 1975; p 163.

(15) Ball, M.; Gilberz, A.; Kropf, H. *Liebigs Ann. Chem.* **1974**, 1013–1015.

(16) The fate of the low molecular weight alkyl radicals formed in the β-scission reactions has not been determined. Further studies are under way to determine the final products of the alkyl radicals.

(17) For a recent review on sulfinyl radicals, see: Chatgilialoglu, C. Sulfinyl Radicals. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Raappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988; Chapter 24, pp 1081–1087. For a recent review on sulfonyl radicals, see: Chatgillialoglu, C. Sulfonyl Radicals. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988; Chapter 24, pp 1088–1087.

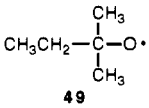
is observed in the photooxidation of **15a,b**, it is believed that the sulfone is derived only from the photooxidation of the intermediate sulfoxides. No sulfone formation is observed in the photooxidation of **15c** and **21**. These observations suggest that the formation of **41** is not competitive with the other processes available to **34**. The difference between the presently observed behavior and that observed earlier must be due to the presence of the 4-nitro group on the aromatic ring.

Comments on Product Formation from Specific Alkyl 4-Nitrophenyl Sulfide Systems. The carbonyl compounds can be formed directly from the photooxidation of either the sulfide or the sulfoxide, or both.

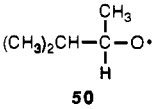
In certain systems it appears that the carbonyl compounds are derived only from the sulfide. The corresponding sulfoxide was not observed to be formed during the course of the photooxidation reaction, and the sulfone and sulfonate are also not formed. Examples of such systems are the *tert*-alkyl 4-nitrophenyl sulfides **25a,b** and **26**. Product formation from these substrates must occur only *via* pathway A shown in Scheme 1. The rate of the heterolytic cleavage of the C–S bond in the peroxysulfoxide intermediates **34** must be accelerated by the steric congestion present in these intermediates relative to the rate of reaction with another molecule of the sulfide **33** which must suffer retardation due to steric factors. In addition, the rate of the heterolytic cleavage of the C–S bond must be accelerated by the relatively stable tertiary and benzylic carbocations formed.

Carbonyl compound formation in other systems appears to occur by the photooxidation of both the sulfide and the sulfoxide. Evidence in support of both pathways being operative is the observation of the formation of the sulfoxide as an intermediate in the oxidation of the sulfide, which reaches a maximum concentration and undergoes photooxidation to the carbonyl compounds, and differences in the distribution of the carbonyl compounds when starting independently from the sulfide and the sulfoxide. Examples of the former are the sulfides **15a,b**, **21**, and **29**, and an example of the latter is the difference in the carbonyl product distributions derived from the photooxidation of sulfide **29** (see eq 10) and the sulfoxide **30** (see Table 1). The alkyl groups in these sulfides are primary and secondary alkyl groups which provide less steric hindrance to attack by a second molecule of the sulfide **33** and less steric destabilization and carbocation stabilization in the heterolytic cleavage of the C–S bond in the peroxysulfoxide intermediates **34**. Although a primary alkyl sulfide, **29** undergoes extensive reaction via pathway A in Scheme 1, suggesting that the heterolytic cleavage and formation of a carbocationic intermediate might be concerted to produce an intermediate phenonium ion which can collapse to form the persulfenate **37** by C–O bond formation at either carbon atom.

Formation of the Carbonyl Compounds. In the photooxidation of **26**, acetone and 2-butanone are the expected products to be formed by the β-scission of the unrearranged alkoxy radical **49**. The relative rate of β-scission of alkoxy radicals, in part, increases with increasing stability of the extruded radical,[18] thus favoring the formation of acetone which is what is experimentally observed. The 3-methyl-2-butanone is formed from the "rearranged" alkoxy radical **50** by hydrogen atom transfer to the sulfinyl radical, while the acetaldehyde is formed by β-scission of **50** with extrusion of the isopropyl radical.

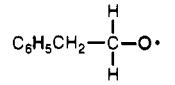


49

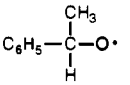


50

In the photooxidation of **29**, the phenylacetaldehyde is formed by hydrogen atom abstraction from the alkoxy radical **51**. The acetophenone is formed by the hydrogen atom transfer from the rearranged alkoxy radical **52**, while the benzaldehyde is formed by β-scission with loss of a methyl radical.[16]



51



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Summary

The observations reported in the present article indicate that the photooxidation chemistry of sulfur-containing compounds is much more rich than previously thought and, with alkyl aryl sulfides, depends critically on the nature of the alkyl group and any substituent attached to the aromatic ring. The further photooxidation of the 4-nitrophenyl sulfoxides, compared to the lack of further photooxidation of alkyl phenyl sulfoxides, is attributed to the electron-withdrawing properties of the 4-nitro group, making the sulfur atom more electrophilic and prone to react with $^1O_2$.

Experimental Section

General Procedure for the Synthesis of Alkyl 4-Nitrophenyl Sulfides. To a solution of 5 mmol of 4-nitrobenzenethiol and 0.2 g (5 mmol) of sodium hydroxide in 15 mL of ethanol in a 50-mL flask was added 5 mmol of the alkyl halide. The reaction mixture was stirred at room temperature for 12 h. Water (15 mL) was added to the reaction mixture, and the resulting mixture was transferred into a separatory funnel and was extracted with 30 mL of ether. The organic layer was separated and washed with saturated aqueous potassium carbonate (3 × 20 mL) and saturated aqueous ammonium chloride (3 × 20 mL). The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give the sulfide which was purified by liquid column chromatography on silica gel using an eluent system composed of Skellysolve B and methylene chloride. The yields of the *pri*- and *sec*-alkyl sulfides were >90%. The yields of the *tert*-alkyl sulfides were 5–10%.

Methyl 4-Nitrophenyl Sulfide (12):[19] UV ($CHCl_3$) λ_{max} 345 nm; ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H), 7.25 (d, J = 8.92 Hz, 2 H), 8.10 (d, J = 8.92 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.6, 123.6, 124.7, 144.4, 148.8; HR EIMS calcd for $C_7H_7NO_2S$ m/e 169.020, found m/e 169.018.

Ethyl 4-Nitrophenyl Sulfide (15a): dark yellow solid; mp 42–43 °C; UV ($CHCl_3$) λ_{max} 344 nm (ϵ = 23 000); ^1H NMR ($CDCl_3$) δ 1.40 (t, J = 7.38 Hz, 3 H), 3.00 (q, J = 7.38 Hz, 2 H), 7.35 (d, J = 8.93 Hz, 2 H), 8.10 (d, J = 8.93 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 25.8, 123.7, 125.8, 144.6, 147.8; HR EIMS calcd for $C_8H_9NO_2S$ m/e 183.035, found m/e 183.034.

***n*-Hexyl 4-Nitrophenyl Sulfide (15b)**: dark yellow liquid; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 0.9 (t, J = 7.03 Hz, 3 H), 1.20–1.50 (m, 6 H), 1.75 (m, 2 H), 3.00 (t, J = 7.32 Hz, 2 H), 7.30 (d, J = 9.00 Hz, 2 H), 8.10 (d, J = 9.00 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.1, 28.1, 28.2, 31.0, 32.3, 124.5, 126.2, 144.8, 147.9; HR EIMS calcd for $C_{12}H_{17}NO_2S$ m/e 239.0979, found m/e 239.0979.

Benzyl 4-Nitrophenyl Sulfide (15c): dark yellow solid; mp 122–125 °C; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 4.23 (s, 2 H), 7.30 (d, J = 8.86 Hz, 2 H), 7.20–7.40 (m, 5 H), 8.05 (d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 36.8, 123.8, 126.4, 127.7, 128.6, 128.7, 135.3, 145.0, 147.2; HR EIMS calcd for $C_{13}H_{11}NO_2S$ m/e 245.051, found m/e 245.052.

2-Propyl 4-Nitrophenyl Sulfide (21): dark yellow liquid; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 1.40 (d, J = 6.67 Hz, 6 H), 3.60 (m, 1 H), 7.35 (d, J = 8.92 Hz, 2 H), 8.15 (d, J = 8.92 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.7, 36.5, 123.9, 127.6, 145.1, 147.2; HR EIMS calcd for $C_9H_{11}NO_2S$ m/e 197.052, found m/e 197.051.

2-Methyl-2-propyl 4-Nitrophenyl Sulfide (25a): viscous dark yellow liquid; UV ($CHCl_3$) λ_{max} 344 nm (ϵ = 10 200 cm^{-1} M^{-1}); ^1H NMR ($CDCl_3$) δ 1.35 (s, 9 H), 7.70 (d, J = 8.81 Hz, 2 H), 8.20 (d, J = 8.81 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.1, 47.5, 123.3, 136.8, 142.3, 147.7; HR EIMS calcd for $C_{10}H_{13}NO_2S$ m/e 211.067, found m/e 211.066.

2-Methyl-2-butyl 4-Nitrophenyl Sulfide (26): dark yellow solid; mp 115–117 °C; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.40 Hz, 3 H), 1.25 (s, 6 H), 1.52 (q, J = 7.40 Hz), 7.65 (d, J = 8.86 Hz, 2 H), 8.20 (d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 9.2,

(18) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(19) Commercially available from Aldrich Chemical Co.

28.4, 35.1, 51.7, 123.3, 136.9, 142.2, 147.6; HR EIMS calcd for $C_{11}H_{15}NO_2S$ *m/e* 225.082, found *m/e* 225.082.

2-Phenyl-2-propyl 4-Nitrophenyl Sulfide (25b). To 15 mL of 48% hydrochromic acid cooled in an ice bath was slowly added with stirring 3.20 g of 2-phenyl-2-propanol. The reaction mixture was allowed to warm to room temperature and then was extracted with 30 mL of ether. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 3.0 g of 2-phenyl-2-propyl bromide, which was purified by distillation under reduced pressure (55–70 °C at 1.8 mmHg). The 2-phenyl-2-propyl bromide was converted to the sulfide as described in the general procedure given above: viscous dark yellow liquid; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 7.15 (d, J = 8.92 Hz, 2 H), 7.30 (m, 5 H), 7.95 (d, J = 8.92 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.1, 52.5, 123.1, 126.4, 127.0, 128.3, 134.0, 143.2, 145.5, 146.9; HR EIMS calcd for $C_{15}H_{15}NO_2S$ *m/e* 273.082, found *m/e* 273.082.

2-Phenylethyl 4-Nitrophenyl Sulfide (29): dark yellow solid; mp 46–48 °C; UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 2.98 (t, J = 8.13 Hz, 2 H), 3.25 (t, J = 8.13 Hz, 2 H), 7.20–7.40 (m, 5 H), 7.30 (d, J = 8.94 Hz, 2 H), 8.10 (d, J = 8.84 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.2, 34.7, 123.8, 126.4, 126.7, 128.4, 128.5, 139.1, 144.8, 147.3; HR EIMS calcd for $C_{14}H_{13}NO_2S$ *m/e* 259.067, found *m/e* 259.066.

General Procedure for the Synthesis of the Alkyl 4-Nitrophenyl Sulfoxides. To a stirred solution of 5 mmol of the alkyl 4-nitrophenyl sulfide in 50 mL of methylene chloride at 0 °C was added dropwise a solution of 1.6 g (5 mmol) of 55% *m*-chloroperbenzoic acid in 30 mL of methylene chloride. After addition the reaction was stirred at 0 °C for 1 h. The reaction mixture was transferred to a separatory funnel. Any remaining peracid was destroyed by washing with 10% sodium sulfite solution until a starch–iodide test was negative. The layers were separated, the organic layer was washed with saturated sodium chloride solution (2 × 30 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The resulting reaction mixtures were chromatographed on silica gel, the sulfones, formed by overoxidation, being eluted with a 4:1 mixture of Skelly Solve F–methylene chloride. The sulfoxides were eluted using ethyl acetate.

Methyl 4-Nitrophenyl Sulfoxide (13): UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$) δ 2.80 (s, 3H), 7.90 (d, J = 8.8 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H); HR EIMS calcd for $C_7H_7NO_3S$ *m/e* 185.015, found *m/e* 185.015.

Ethyl 4-Nitrophenyl Sulfoxide (17a): yellow liquid; UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$), δ 1.25 (t, J = 7.40 Hz, 3 H), 2.80 (dq, J = 13.49 Hz, J = 7.34 Hz, 1 H), 3.05 (dq, J = 13.49 Hz, J = 7.39 Hz, 1 H), 7.80 (d, J = 8.84 Hz, 2 H), 8.40 (d, J = 8.84 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 5.6, 50.1, 124.2, 125.2, 149.4, 150.9; HR EIMS calcd for $C_8H_9NO_3S$ *m/e* 199.0303, found *m/e* 199.030.

***n*-Hexyl 4-Nitrophenyl Sulfoxide (17b)**: yellow liquid; UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$), δ 0.87 (t, J = 6.80 Hz, 3 H), 1.25–1.90 (m, 6 H), 2.85 (m, 2 H), 7.84 (d, J = 8.92 Hz, 2 H), 8.40 Hz (d, J = 8.92 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 21.7, 22.2, 28.1, 31.1, 56.9, 124.1, 124.9, 149.2, 151.6; HR EIMS calcd for $C_{12}H_{17}NO_3S$ *m/e* 255.093, found *m/e* 255.094.

Benzyl 4-Nitrophenyl Sulfoxide (17c): yellow solid; mp 165–167 °C; UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$) δ 4.03 (d, J = 20.46 Hz, 2 H), 4.06 (d, J = 20.46 Hz, 1 H), 7.00–7.40 (m, 5 H), 7.50 (d, J = 8.86 Hz, 2 H), 8.25 (d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 63.0, 123.7, 125.5, 127.8, 128.6, 128.7, 130.2, 149.4, 150.1; HR FAB calcd for ($C_{13}H_{11}NO_3S$ + H^+) *m/e* 262.054, found *m/e* 262.053.

2-Propyl 4-Nitrophenyl Sulfoxide (22): yellow liquid; UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 6.76 Hz, 3 H), 1.35 (d, J = 6.93 Hz, 3 H), 2.95 (m, 1 H), 7.80 (d, J = 8.86 Hz, 2 H), 8.40 (d, J = 8.86 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.3, 16.1, 54.8, 123.7, 125.9, 149.4, 149.6; HR EIMS calcd for $C_9H_{11}NO_3S$ *m/e* 213.046, found *m/e* 213.046.

2-Phenylethyl 4-Nitrophenyl Sulfoxide (30): yellow liquid; UV ($CHCl_3$) λ_{max} 300 nm; ^1H NMR ($CDCl_3$) δ 2.90 (m, 1 H), 3.05 (m, 1 H), 3.10 (m, 1 H), 7.10–7.20 (m, 5 H), 7.90 (d, J = 8.63 Hz, 2 H), 8.40 (d, J = 8.63 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0, 58.2, 124.2, 124.9, 126.8, 128.4, 128.8, 137.9, 149.3, 151.2; HR FAB calcd for ($C_{14}H_{13}NO_3S$ + H^+) *m/e* 276.069, found *m/e* 276.069.

General Procedure for the Synthesis of the Alkyl 4-Nitrophenyl Sulfones. To a stirred solution of 5 mmol of the alkyl 4-nitrophenyl sulfide in 50 mL of methylene chloride at 0 °C was added dropwise a solution of 3.2 g (10 mmol) of 55% *m*-chloroperbenzoic acid in 30 mL of methylene chloride. After addition the reaction was stirred at 0 °C for 1 h. The reaction mixture was transferred to a separatory funnel. Any remaining peracid was destroyed by washing with 10% sodium sulfite solution until a starch–iodide test was negative. The layers were separated, the organic layer was washed with saturated sodium chloride solution (2 × 30 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The resulting reaction mixtures were then chromatographed on silica gel, the sulfones being eluted using 4:1 Skelly Solve F–CH_2Cl_2.

Methyl 4-Nitrophenyl Sulfone: UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 3.15 (s, 3 H), 8.20 (d, J = 8.74 Hz, 2 H), 8.40 (d, J = 8.74 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.2, 124.5, 128.9, 145.8, 150.7; HR EIMS calcd for $C_7H_7NO_4S$ *m/e* 201.009, found *m/e* 201.008.

Ethyl 4-Nitrophenyl Sulfone (19a): white solid; mp 135–137 °C; UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7.41 Hz, 3 H), 3.40 (q, J = 7.41 Hz, 2 H), 8.15 (d, J = 8.94 Hz, 2 H), 8.45 (d, J = 8.94 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 7.2, 50.5, 124.4, 129.7, 144.1, 150.8; HR EIMS calcd for $C_8H_9NO_4S$ *m/e* 215.025, found *m/e* 215.023.

1-Hexyl 4-Nitrophenyl Sulfone (19b): colorless liquid; UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.05 Hz, 3 H), 1.25–1.45 (m, 6 H), 1.75 (m, 2 H), 3.10 (m, 2 H), 8.15 (d, J = 8.87 Hz, 2 H), 8.45 (d, J = 8.87 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 22.3, 27.6, 30.9, 55.9, 124.3, 129.4, 144.6, 150.6; HR EIMS calcd for $C_{12}H_{17}NO_4S$ *m/e* 271.088, found *m/e* 271.087.

Benzyl 4-Nitrophenyl Sulfone (19c): white solid; mp 168–170 °C; UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.05 (m, 5 H), 7.80 (d, J = 8.59 Hz, 2 H), 8.25 (d, J = 8.59 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 63.1, 123.9, 127.1, 128.9, 129.3, 130.2, 130.7, 143.3, 150.7; HR EIMS calcd for $C_{13}H_{11}NO_4S$ *m/e* 277.041, found *m/e* 277.042.

2-Propyl 4-Nitrophenyl Sulfone (23): white solid; mp 120–122 °C; UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 1.34 (d, J = 6.84 Hz, 6 H), 3.25 (m, 1 H), 8.10 (d, J = 8.87 Hz, 2 H), 8.41 (d, J = 8.87 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.0, 55.8, 124.2, 130.5, 142.8, 150.8; HR EIMS calcd for $C_9H_{11}NO_4S$ *m/e* 229.041, found *m/e* 229.040.

2-Phenylethyl 4-Nitrophenyl Sulfone (31): white solid; mp 118–120 °C; UV ($CHCl_3$) λ_{max} 251 nm; ^1H NMR ($CDCl_3$) δ 3.10 (m, 2 H), 3.45 (m, 2 H), 7.05–7.15 (m, 5 H), 8.05 (d, J = 8.94 Hz, 2 H), 8.40 (d, J = 8.94 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.5, 57.5, 124.4, 127.1, 128.2, 128.8, 129.5, 136.6, 144.6, 150.7; HR EIMS calcd for $C_{14}H_{13}NO_4S$ *m/e* 291.056, found *m/e* 291.057.

General Procedure for the Preparation of Alkyl 4-Nitrobenzenesulfonates. To a solution of 5 mmol (0.12 g) of sodium hydride in 20 mL of anhydrous THF was added slowly at 0 °C 5 mmol of alcohol. The reaction was then stirred for another 10 min, after which 5 mmol (0.96 g) of 4-nitrobenzenesulfonyl chloride was added slowly and portionwise. The reaction was followed by thin-layer chromatography. After completion 10 mL of icy-cold water was added slowly. The layers were separated, and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and whenever it was possible, the sulfonate was purified by chromatography on silica gel using an eluent system composed of Skellysolve B and methylene chloride. The sulfonates underwent decomposition on attempts to determine their melting points.

Ethyl 4-Nitrobenzenesulfonate (20a): white solid; ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 7.15 Hz, 3H), 4.20 (q, J = 7.15 Hz, 3 H), 8.10 (d, J = 8.77 Hz, 2 H), 8.45 (d, J = 8.77 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.7, 68.1, 124.4, 129.1, 142.0, 150.6; HR CIMS (isobutane) calcd for ($C_8H_9NO_5S$ + H^+) *m/e* 232.028, found *m/e* 232.027.

1-Hexyl 4-Nitrobenzenesulfonate (20b): white solid; mp ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 6.60 Hz, 3 H), 1.30 (m, 6 H), 1.60 (m, 2 H), 4.06 (t, J = 6.55 Hz, 2 H), 8.05 (d, J = 8.89 Hz, 2 H), 8.40 (d, J = 8.89 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.3, 24.8, 26.7, 30.9, 72.0, 124.4, 129.1, 141.9, 150.6; HR CIMS (isobutane) calcd for $C_{12}H_{17}NO_5S$ *m/e* 288.091, found *m/e* 288.090.

Benzyl 4-Nitrobenzenesulfonate (20c): white solid; H NMR ($CDCl_3$, isolated as a mixture with benzyl alcohol) δ 5.20 (s, 2 H), 7.35 (m, 5 H), 8.00 (d, J = 8.95 Hz, 2 H), 8.35 (d, J = 8.95 Hz, 2 H). No parent ion could be observed by EIMS or CIMS.

2-Propyl 4-Nitrobenzenesulfonate (24). White solid: ^1H NMR ($CDCl_3$), δ 1.36 (d, J = 6.27 Hz, 6 H), 4.95 (m, 1 H), 8.30 (d, J = 8.88 Hz, 2 H), 8.55 (d, J = 8.88 Hz, 2 H); ^{13}C NMR ($CDCl_3$), δ 22.6, 79.2, 125.0, 128.4, 148.3, 151.2; HR CIMS (isobutane) calcd for ($C_9H_{11}NO_5S$ + H^+) *m/e* 246.044, found 246.043.

2-Phenethyl 4-Nitrobenzenesulfonate (32): white solid; ^1H NMR ($CDCl_3$) δ 3.00 (t, J = 6.63 Hz, 2 H), 4.40 (t, J = 6.63 Hz, 2 H), 7.05–7.15 (m, 5 H), 7.90 (d, J = 8.82 Hz, 2 H), 8.25 (d, J = 8.82 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.0, 72.5, 124.2, 126.9, 128.5, 128.8, 128.9, 135.8, 141.4, 150.4; HR CIMS (isobutane) calcd for ($C_{12}H_{17}NO_5S$ + H^+) *m/e* 288.091, found *m/e* 288.090.

General Procedure for the $^1O_2$ Photooxidation of the Alkyl 4-Nitrophenyl Sulfides and Sulfoxides. A Rayonet photochemical chamber reactor,

model RPR-100 equipped with 350-nm lamps was used to irradiate the sample solutions. The temperatures of the reaction solutions were maintained at ~35 °C by a cooling fan. A conical flask containing a 5×10^{-3} M solution of the sulfide or sulfoxide in $CDCl_3$ was irradiated under an oxygen atmosphere. Portions of the reaction solutions were periodically removed, and the NMR spectra were recorded. As the reactions progressed, the solutions turned slightly cloudly with the formation of a precipitate. After completion of the reactions, the $CDCl_3$ solutions were removed from the flask and the flask was washed with acetone-d_6. The NMR spectra of the acetone-d_6 rinses were recorded, showing the presence of only 4-nitrobenzenesulfonic acid.[20]

The products formed in the photooxidation reactions were identified directly by comparison of their ^1H NMR spectral characteristics with those of authentic samples of the sulfoxides, sulfones, sulfonates, and carbonyl compounds. The relative yields of the products were determined by the integration of the ^1H NMR spectra of the product mixtures.

Preparation of 2-Deuterio-2-propyl 4-Nitrophenyl Sulfide. Synthesis of 2-Deuterio-2-propanol.[21] In a three-necked flask containing 20 mL of anhydrous diethyl ether and 10 mmol (0.74 mL) of acetone was added at 0 °C slowly and portionwise 0.4 g of sodium borodeuteride. The reaction mixture was heated to reflux for 1 h. The reaction was cooled to 20 °C and was carefully transferred to a separatory funnel. Saturated aqueous sodium chloride (20 mL) was added. The layers were separated, and the organic layer was dried over magnesium sulfate and filtered through a cotton plug. Careful distillation afforded a 90% yield of 2-deuterio-2-propanol.

Synthesis of 2-Deuterio-2-propyl 4-Nitrophenyl Sulfide (21-*2-d*). To a solution of 5 mmol (0.38 mL) of 2-deuterio-2-propanol and 3 mL of pyridine at 0 °C in a three-necked flask was slowly added 5.5 mmol (1.05 g) of *p*-toluenesulfonyl chloride. The mixture was stirred for 2 h at room temperature. Cold hydrochloric acid (20 mL, 3%) was carefully added to the reaction mixture. Dichloromethane (50 mL) was added, and the entire solution was transferred to a separatory funnel. The layers were separated, and the organic layer was dried over magnesium sulfate. The solution was filtered, concentrated under reduced pressure, and immediately reacted with sodium 4-nitrophenyl thiolate as described above for the synthesis of the sulfides giving **21-*2-d*** (75%) as a dark yellow liquid: UV ($CHCl_3$) λ_{max} 344 nm; ^1H NMR ($CDCl_3$) δ 1.35 (s, 6 H), 7.40 (d, J = 8.89 Hz, 2 H), 8.10 (d, J = 8.89 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.4, 36.0 (t, $J_{^{13}C^2H}$ = 86.1 Hz, 1 C), 123.7, 127.4, 144.9, 147.1; HR FAB calcd for ($C_9H_{10}DNO_2S + H^+$) m/e 198.057, found m/e 198.064.

Measurement of the Kinetic Isotope Effect. The same experimental conditions described previously for the photooxidation of the alkyl 4-nitrophenyl sulfides were employed. A 1:1 ratio of 2-deuterio-2-propyl 4-nitrophenyl sulfide and 2-propyl 4-nitrophenyl sulfide in presence of 1 equiv of anisole (as an internal standard) in $CDCl_3$ was irradiated under an atmosphere of oxygen. Aliquots of the reaction mixture were periodically removed and the ^1H NMR spectrum was recorded. The relative rates of disappearance of **21** and **21-*2-d*** were determined from the integral of the 2-hydrogen in **21** versus the methyl doublet and the methyl resonance of the anisole. The k_H/k_D was calculated using the following formula: $k_H/k_D = [\log H/H_0]/[\log D/D_0]$ where H and D represent respectively the concentrations of the protio and the deuterio species.[22]

Supplementary Material Available: Figures showing ^1H NMR spectra (53 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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