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C–S bond cleavage in the sensitized photooxygenation of *tert*-alkyl phenyl sulfides. The role of superoxide anion

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Abstract—The *N*-methylquinolinium tetrafluoroborate (NMQ$^+$)-photosensitized oxidation of *tert*-alkyl phenyl sulfides **1a**–**c** (**1a**, *tert*-alkyl=*tert*-butyl; **1b**, *tert*-alkyl=2-phenyl-2-propyl; **1c**, *tert*-alkyl=1,1-diphenylethyl) and benzyl phenyl sulfide (**2**) were investigated in CH_3CN by nanosecond laser flash photolysis (LFP) and steady-state irradiation either under nitrogen or in the presence of O_2. By laser irradiation, the formation of sulfide radical cations **1a**$^{+\bullet}$–**c**$^{+\bullet}$ in the monomeric form (λ_{max}=520 nm) and of **2**$^{+\bullet}$ in both the monomeric (λ_{max}=520 nm) and dimeric form (λ_{max}=780 nm) were observed within the laser pulse. In both cases, the radical cations decayed by second-order kinetics without any apparent formation of transients attributable to C–S bond rupture. In line with these results, very small amounts of photoproducts were obtained under nitrogen thus suggesting that the sulfide radical cations mainly undergo a back electron transfer process with the reduced *N*-methylquinolinium (NMQ$^\bullet$). A different situation was found in the presence of O_2 since steady-state photolysis produced substantial amounts of C–S bond cleavage products (alcohols, alkenes, and ketones from **1a**–**c** and benzaldehyde from **2**), in contrast with LFP experiments. Formation of products was, however, significantly reduced in the presence of benzoquinone, a trap for $O_2^{-\bullet}$ generated by NMQ$^\bullet$ and O_2. For the *tert*-alkyl phenyl sulfides, **1a**–**c**, these results have been interpreted by suggesting that C–S bond cleavage products in the presence of oxygen mostly derive from the decomposition of a thiadioxirane **6** formed by the reaction of the sulfide radical cation with $O_2^{-\bullet}$. In this cleavage a sulfinate and a carbocation formed. The former is oxidized to sulfonate, whereas the carbocation can react with adventitious water to form the alcohol (and the alkene therefrom) and with $O_2^{-\bullet}$ to produce the ketone. For **2** (a sulfide with α-CH bonds) probably a different mechanism holds, benzaldehyde coming from the α-phenylthio carbon radical formed from deprotonation by $O_2^{-\bullet}$ of **2**$^{n+\bullet}$.

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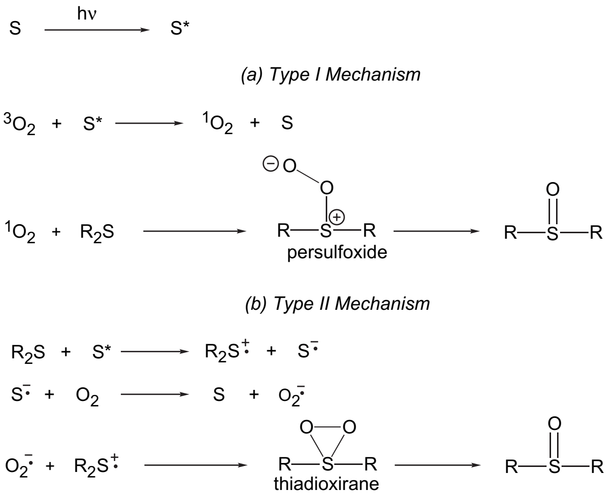
1. Introduction

The sensitized photooxygenation of organic sulfides is receiving continuous attention for the important biological implications as well as the possible practical applications in organic synthesis.[1–14] Two different mechanisms have been suggested for this process.[15,16] The Type I mechanism involves the intervention of $^1O_2$ generated by the reaction of the excited sensitizer with $^3O_2$ (henceforth simply indicated as O_2), whereas in the Type II mechanism the excited sensitizer abstracts an electron from the substrate forming a radical cation that then reacts with $O_2^{-\bullet}$ formed by O_2 and the reduced form of the sensitizer. Recent work has presented evidence indicating that the two mechanisms involve different intermediates, namely a persulfoxide in the Type I mechanism and a thiadioxirane in the Type II mechanism (Scheme 1).[15,16]



Scheme 1.

In both mechanisms, sulfoxides are generally the main products. However, variable amounts of C–S bond cleavage products can also be obtained, depending on the substrate

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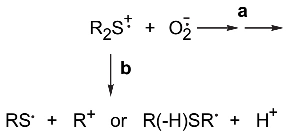
structure. The formation of these products has been discussed in some detail for the Type I mechanism, where they are suggested to be derived by additional pathways available to the persulfoxide intermediate.[10,11] In the electron transfer mechanism the fragmentation products are attributed to possible reactions of the sulfide radical cation involving the cleavage of a C–S or an α-C–H bond, in competition with the reaction with $O_2^{-\bullet}$ leading to sulfoxide (Scheme 2).[13,17]



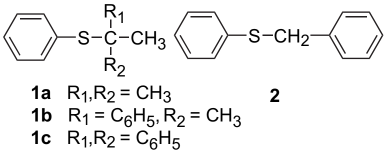
$$R_2S^{+\bullet} + O_2^{-\bullet} \xrightarrow{a} R_2SO$$

$$\downarrow b$$

$$RS^{\bullet} + R^+ \text{ or } R(\text{-}H)SR^{\bullet} + H^+$$

Scheme 2.

In view of the importance of sulfides photooxygenation, it is certainly of interest to get more information on this problem. Thus, we have carried out a detailed investigation of the photochemical oxygenation of *tert*-alkyl phenyl sulfides **1a–c** sensitized by *N*-methylquinolinium tetrafluoroborate (NMQ^+) in CH_3CN. These reactions, that exclusively lead to fragmentation products, have been studied by nanosecond laser flash photolysis (LFP) and steady-state photolysis and the transient species produced, their decay pathways, and the final photoproducts have been identified. The results of this study, reported herewith, have led to the important conclusion that the main pathway for the formation of fragmentation products is not the direct C–S bond cleavage in the radical cation, but the reaction of the sulfide radical cation with the superoxide anion generated in the reaction of $NMQ^{\bullet}$ with oxygen. For comparison purposes, the photolysis of benzyl phenyl sulfide (**2**) has also been investigated. Fragmentation products are formed in this case too, but the mechanism is probably different than that proposed for the *tert*-alkyl phenyl sulfides.

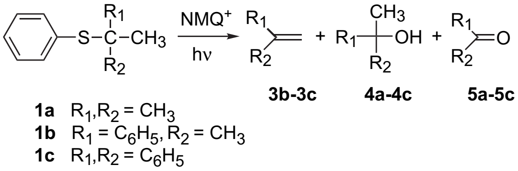


2. Results

2.1. Steady-state photolysis

The steady-state photooxidations sensitized by NMQ^+ were carried out in air-saturated CH_3CN or for comparison purpose under N_2. No reaction was observed in the absence of the sensitizer. The reaction products were identified by GC–MS and ^1H NMR (comparison with authentic specimens, see Section 5).

Photolysis in the presence of O_2. Under air, quite efficient photochemical processes were observed with **1a–c**. Fragmentation products were obtained exclusively in the photoirradiation of *tert*-alkyl phenyl sulfides **1a–c** with quantum yields (Φ) between 0.3 and 0.5 for the products coming from the alkyl moiety. Benzenesulfonate is the main product derived from the sulfide moiety even though a small amount of diphenyl disulfide was detected. No quantum yields were determined for the sulfur containing products. Alcohols, alkenes, and ketones were the products formed from **1b** and **1c** as described in Scheme 3, where only the products derived from the alkyl moiety are indicated. The corresponding alcohol and ketone were also formed with **1a**. In this case, *N*-*tert*-butylacetamide was also produced, whereas the alkene was not observed.



Scheme 3.

A further notation, however, was that with **1b** and **1c**, the alcohol is progressively converted into alkene as the reaction proceeds, as shown, for example, from the data in Table 1 for the photolysis of **1b**.

Table 1. Quantum yields of the photoproducts formed in the oxidation of 2-phenyl-2-propyl phenyl sulfide (**1b**) photosensitized by NMQ^+ in air-saturated CH_3CN[a]

T (min)	Φ(**3b**)	Φ(**4b**)	Φ(**5b**)	Φ(**3b**)+Φ(**4b**)
60	0.018	0.17	0.10	0.188
90	0.13	0.060	0.086	0.190
120	0.16	0.057	0.096	0.217

[a] [sulfide]=0.01 M. $[NMQ^+]=3.4\times10^{-3}$ M.

Accordingly, it can be seen that whereas the overall quantum yield is substantially independent of irradiation time, those of the alkene **3b** and the alcohol **4b** increase and decrease, respectively, by increasing the irradiation time. However, the sum Φ(**3b**)+Φ(**4b**) remains almost constant. Most likely, alcohol is the primary product and there is a substantial and increasing conversion of the alcohol into the alkene, probably promoted by H^+ formed during the photolysis. Thus, in Table 2, where the results for all *tert*-alkyl phenyl sulfides are depicted, we report the Φ value for the ketone and the overall quantum yield, Φ(**3**)+Φ(**4**), of alkene and alcohol for **1b** and **1c**. In the same Table the results of the steady-state photolysis of benzyl phenyl sulfide that leads to benzyl phenyl sulfoxide and a fragmentation product, benzaldehyde, are also reported. The possible role of $O_2^{-\bullet}$, that forms in the reaction with $NMQ^{\bullet}$ (Scheme 1b, $S=NMQ^+$), was investigated by performing the photolysis in the presence of benzoquinone, a well known trap for $O_2^{-\bullet}$.[18] A very significant drop in the product quantum yields was observed, particularly with **1a** and **1b** (Table 2).

When the above reactions were carried out *in the absence of oxygen* (flushing the solutions with N_2 before irradiation) no products were observed with the NMQ^+/**1a** and NMQ^+/**2** systems and a substantial decrease (about one order of magnitude) in quantum yields was observed with the sulfides **1b** and **1c**. Under these conditions, diphenyl disulfide was also

Table 2. Quantum yields of the photoproducts formed in the oxidation of *tert*-alkyl phenyl sulfides (**1a**–**c**) and benzyl phenyl sulfide (**2**) photosensitized by NMQ^+ in CH_3CN[a]

Substrate		Quantum yields[b]		
		Φ_{TOT}	$\Phi(\mathbf{3})+\Phi(\mathbf{4})$	$\Phi(\mathbf{5})$
1a	Air	0.36	0.085[c]	0.21
	Air[d]	—[e]	—[e]	—[e]
	N_2	—[e]	—[e]	—[e]
1b	Air	0.29	0.19	0.10
	Air[d]	0.015	0.007	0.008
	N_2	0.038	0.038	—
1c	Air	0.44	0.31	0.13
	Air[d]	0.13	0.087	0.043
	N_2	0.058	0.058	—[e]
			$\Phi(PhCH_2SOPh)$	$\Phi(PhCHO)$
2	Air	0.14	0.03	0.11
	Air[d]	—[e]	—[e]	—[e]
	N_2	—[e]	—[e]	—[e]

[a] [sulfide]=1.0×10^{-2} M, [NMQ^+]=1.0×10^{-2} M under nitrogen and [NMQ^+]=3.4×10^{-3} M in air-saturated condition. Quantum yields are determined after 1 h irradiation.

[b] Quantum yields of all the products from the alkyl moiety. The error is ±10%.

[c] *N-tert*-butylacetamide (Φ=0.065) is also formed.

[d] In the presence of 1.2×10^{-3} M *p*-benzoquinone.

[e] Under the detection limit (Φ<0.001).

formed, whereas no formation of the ketone **5** was observed. These results are also displayed in Table 2.

Finally, since excited NMQ^+ can also react with O_2 to form $^1O_2$,[15] we tested the reactivity of our sulfides toward $^1O_2$. Thus, the photolysis of **1b** was carried out in the presence of Rose Bengal in O_2-saturated CH_3CN.[19] No detectable amounts of photoproducts were obtained after 30 min of irradiation.

2.2. Fluorescence quenching

Fluorescence quenching experiments were carried out in air-saturated CH_3CN to determine the efficiency by which substrates **1a**–**c** and **2** quench the lowest excited singlet state of NMQ^+. The fluorescence intensity of NMQ^+ was recorded by steady-state experiments in the absence ($I°$) and in the presence (I) of increasing concentrations of the substrates **1a**–**c** and **2**. The second-order rate constants for NMQ^+ fluorescence quenching (k_q) were calculated from the slopes of the linear Stern–Volmer plots ($I°/I$ vs [**1a**–**c**, **2**]) divided by the lifetime of $^1NMQ^{+*}$ (20 ns)[20] (Fig. S1 and Table S1 in the Supplementary data). The Stern–Volmer plots show that all the substrates quench the emission of NMQ^+ with rate constants, which are close to the diffusion limit (1.5–1.8×10^{10} M^{-1} s^{-1}).[21]

2.3. Laser flash photolysis studies

The laser photolysis experiments (λ_{exc}=355 nm) were carried out in CH_3CN under N_2- and O_2-saturated conditions in the presence of 1 M toluene, which was used as cosensitizer to reduce the efficiency of the back electron transfer process and, consequently, to increase the concentration of the transient formed within the laser pulse.[22] By laser photolysis of the NMQ^+/toluene/**1a**–**c** systems in N_2-saturated solutions, similar time-resolved absorption spectra were observed. Two absorption bands were detected just after the laser pulse in the 400 and 520 nm regions (time-resolved absorption spectra for the NMQ^+/toluene/**1a** system are reported in Fig. 1a, time-resolved absorption spectra for the NMQ^+/toluene/**1b** and NMQ^+/toluene/**1c** systems are reported in Figs. S2 and S3 in the Supplementary data). These bands were assigned to $NMQ^•$ (λ_{max}=400 and 550 nm)[23] and the sulfide radical cations in the monomeric form (λ_{max}=520 nm).[24]

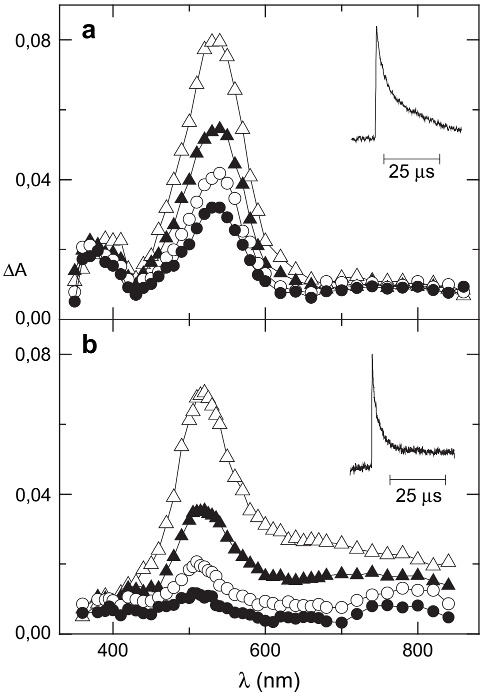


Figure 1. Time-resolved absorption spectra of the NMQ^+ (3.4×10^{-3} M)/toluene (1 M)/$(CH_3)_3CSPh$ (1.0×10^{-2} M) system in CH_3CN: (a) N_2-saturated, recorded 0.2 (△), 4.8 (▲), 10 (○) and 16 (●) μs after the laser pulse; inset: decay kinetics recorded at 520 nm. λ_{exc}=355 nm. (b) O_2-saturated, recorded 0.08 (△), 2.0 (▲), 4.0 (○), 6.1 (●) μs after the laser pulse; inset: decay kinetics recorded at 520 nm. λ_{exc}=355 nm.

Laser photolysis of the NMQ^+/toluene/**2** system under N_2 showed an additional broad absorption band at 780 nm that was assigned to the dimer sulfide radical cation (Fig. 2a).[25] Very reasonably, the dimer was not observed with **1a**–**c** due to the steric hindrance of the *tert*-alkyl group.[26]

The time-evolution of the absorption spectra shows that the decay of the two signals recorded at ca. 400 and 520 nm is not accompanied by the buildup of any transient, which can be assigned to products of C–S bond cleavage, i.e., the phenylthiyl radical $PhS^•$ (λ_{max}=450–490 nm)[27] and, in the case of $\mathbf{1c}^{+•}$, the 1,1-diphenylethyl cation (λ_{max}=420 nm).[28] Moreover, in the LFP experiment with the NMQ^+/toluene/**2** system, analysis of the spectral evolution did not show the growth of the absorption of $PhSCH^•Ph$ (λ_{max}=350 nm),[21] i.e., the product of benzylic C–H deprotonation of $\mathbf{2}^{+•}$. In O_2-saturated solutions, an identical situation was observed, apart from the fact that the time-resolved absorption spectra are modified by the fast decay of $NMQ^•$, that is efficiently quenched by molecular oxygen;[15] thus, the shoulder at ca. 400 nm disappears and the only recorded transient concerns

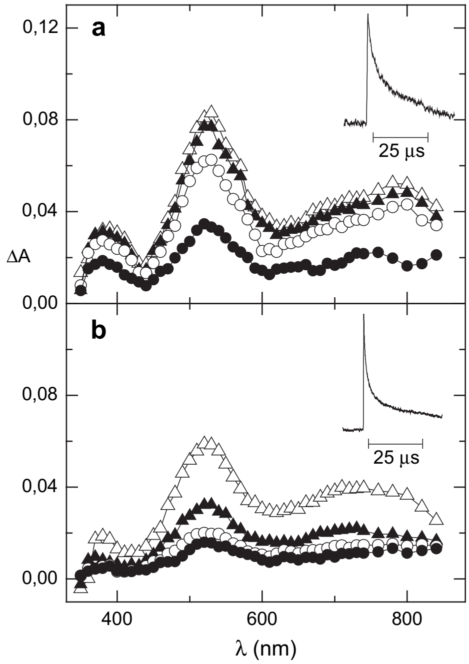


Figure 2. Time-resolved absorption spectra of the NMQ^+ (3.4×10^{-3} M)/ toluene (1 M)/$PhCH_2SPh$ (1.0×10^{-2} M) system in CH_3CN: (a) N_2-saturated, recorded 0.08 (△), 0.32 (▲), 1.0 (○) and 5.8 (●) μs after the laser pulse; (b) O_2-saturated, recorded 0.08 (△), 0.94 (▲), 3.0 (○), 6.0 (●) μs after the laser pulse. Inset: decay kinetics recorded at 530 nm. λ_{exc}=355 nm.

the sulfide radical cation (time-resolved absorption spectra are reported in Fig. 1b and Fig. 2b for the NMQ^+/toluene/ **1a** and NMQ^+/toluene/**2** systems and in Figures S2 and S3 in the Supplementary data for the NMQ^+/toluene/**1b** and NMQ^+/toluene/**1c** systems). The decay rate of radical cations **1a**–**c**$^{+\bullet}$ and **2**$^{+\bullet}$ was determined by following the absorption decay at 520 nm. Under nitrogen and oxygen the decay kinetics followed second-order laws, (see insets in Figs. 1 and 2 for the decay of **1a**$^{+\bullet}$ and **2**$^{+\bullet}$, respectively) and the decay rate constants (k_2) divided by the extinction coefficient (ε), for all the radical cations, measured at 25 °C are reported in Table 3.

It can be observed that the decay rate constants are not significantly influenced by the structure of the sulfide and that the values under oxygen are higher than those observed under nitrogen.

Time-resolved spectra recorded by laser flash photolysis of the NMQ^+/**1b** system in the presence of BQ (9.7×10^{-4} M) in O_2-saturated CH_3CN (see Fig. S4 in the Supplementary data) showed the characteristic absorption band of $BQ^{-\bullet}$ (λ_{max}=520 nm)[29] thus confirming the electron transfer process from $O_2^{-\bullet}$ to BQ.

Table 3. Decay rate constants of **1a**–**c**$^{+\bullet}$ and **2**$^{+\bullet}$ formed by laser photolysis of the NMQ^+ (3.4×10^{-3} M)/toluene (1 M)/**1a**–**c**, **2** (1.0×10^{-2} M) systems in N_2- and O_2-saturated CH_3CN (λ_{ecc}=355 nm)

Sulfide	k_2/ε (10^6 s^{-1} cm)	
	N_2	O_2
1a	4.0	12
1b	2.7	12
1c	5.0	16
2	4.0	15

3. Discussion

3.1. *tert*-Alkyl phenyl sulfides

The observation that sulfides **1a**–**c** quench the fluorescence emission of NMQ^+ with rates close to the diffusion limit indicates that NMQ^+ acts as an electron transfer sensitizer. The high efficiency is certainly related to the reduction potential of $^1NMQ^{+*}$ (2.7 V vs SCE)[22] that is much higher than those of the *tert*-alkyl phenyl sulfide radical cations **1a**$^{+\bullet}$–**c**$^{+\bullet}$ (ca. 1.6 V vs SCE).[17] Any possible contribution of $^1O_2$ to the photooxidation has been shown to be negligible.

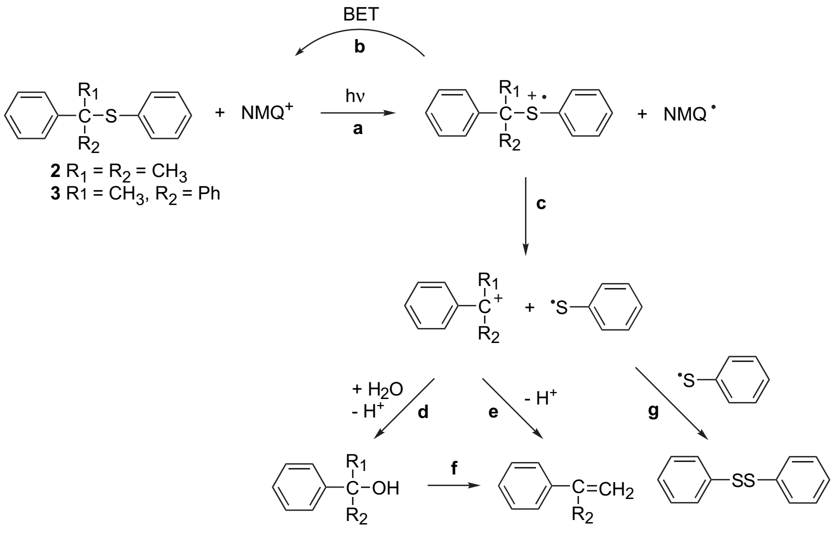
The ET mechanism from the sulfides to $^1NMQ^{+*}$ is also supported by the observation, in the laser flash photolysis experiments of the NMQ^+/toluene/**1a**–**c** systems in N_2-saturated solutions, of absorption bands that have been assigned to $NMQ^\bullet$ (λ_{max}=400 and 550 nm) and the sulfide radical cations (λ_{max}=520 nm). Under oxygen, the only recorded transient is the sulfide radical cation (λ_{max}=520 nm) since $NMQ^\bullet$ is converted to NMQ^+.

However, both under oxygen and nitrogen the decay of the radical cation is not accompanied by the buildup of any transient. Particularly, the transients expected for a direct C–S bond cleavage in the radical cation (phenylthiyl radical in all cases and the tertiary carbocation from **1c**$^{+\bullet}$) were not observed. Since second-order kinetics were followed and the rates are faster under oxygen, the decays are reasonably attributed to back electron transfer, under nitrogen, and to a reaction with $O_2^{-\bullet}$, under oxygen.

The results of steady-state photoirradiations under nitrogen (formation of small amounts of photoproducts with sulfides **1b** and **1c**, and no reaction at all with **1a**) were in substantial agreement with those of the laser photolysis study. The low efficiency observed is fully consistent with a process dominated by back electron transfer in the geminate radical/ radical cation pair (Scheme 4, path b).

The structure of photoproducts formed (alkenes **3b** and **3c** and alcohols **4b** and **4c**, from **1b** and **1c**, respectively) suggests that at least for **1b**$^{+\bullet}$ and **1c**$^{+\bullet}$ a pathway involving the cleavage of the C–S bond, leading to the tertiary benzylic cations and the phenylthiyl radical (Scheme 4, path c) can also operate, albeit as a minor route (not revealable in LFP experiments). The benzylic cations can react with adventitious water to form the alcohols **4** or lose a proton to produce the alkenes **3** (paths d and e in Scheme 4). However, alkenes **3** seem to be formed primarily by acid induced dehydration of the alcohol (Scheme 4, path f, see Section 2). In both cases, dimerization of the phenylthiyl radical leads to diphenyl disulfide. With **1a**$^{+\bullet}$, C–S bond cleavage is probably slower (a less stable carbocation is formed) than with **1b**$^{+\bullet}$ and **1c**$^{+\bullet}$ and cannot compete at all with back electron transfer. Thus, no products are observed in the steady-state photolysis.

However, as shown by the data in Table 2, the efficiency of photolysis of the sulfides **1a**–**c** significantly increases in the presence of oxygen (under air). From **1a**, the alcohol **4a** and *tert*-butylacetamide are formed together with acetone (**5a**). The ketones **5b** and **5c**, the alkenes **3b** and **3c**, and the

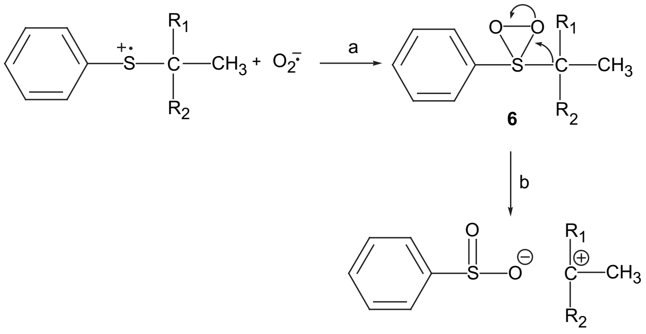


Scheme 4.

alcohols **4b** and **4c**, are formed from **1b** and **1c**, respectively. In all cases, benzenesulfonate is the main product coming from the phenyl sulfide moiety even though small amounts of diphenyl disulfide are observed.

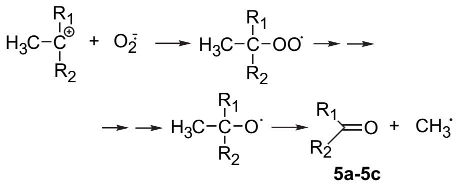
Clearly, the presence of O_2 promotes a fragmentation process that is much more important than that coming from the direct C–S bond cleavage in the radical cation mentioned above. A possible proposal is that the fragmentation products in the presence of oxygen mostly derive from the decomposition of an intermediate formed by the reaction of the radical cation with the superoxide anion generated by $NMQ^{\bullet}$ and O_2. As already mentioned, the reaction of sulfide radical cations with $O_2^{-\bullet}$ is the key step in the electron transfer photoinduced sulfoxidations of sulfides and it is reasonable to suggest that it can play a fundamental role also in the fragmentation reactions investigated. This suggestion is supported by the following. First, as already observed, the presence of oxygen strongly increases the efficiency of the photolysis, producing quantum yields of fragmentation products much higher that those found in the presence of nitrogen. Second, a reaction of $O_2^{-\bullet}$ with the radical cation is indicated by the results of time-resolved experiments. Accordingly, as already noted, the second-order decay of the radical cation in the presence of O_2 is ca. 3–4 times faster than in the presence of nitrogen, being probably determined by the reaction of the radical cation with $O_2^{-\bullet}$, and there is no effect of the sulfide structure on the reactivity. Third and still more significant, in the presence of benzoquinone that can trap $O_2^{-\bullet}$, a substantial drop of the quantum yield in the photolysis of **1a**–**c** under air was observed.[30]

With convincing evidence in hand that the reaction of the sulfide radical cations of **1a**–**c** with $O_2^{-\bullet}$ is en route to fragmentation products, we can try to envisage a reasonable mechanistic scheme. In previous work[15] we have reported evidence indicating that in electron transfer photooxygenations, the reaction of the sulfide radical cation with $O_2^{-\bullet}$ leads to a thiadioxirane **6** (Scheme 5, path a). Usually, the thiadioxirane is expected to react with another sulfide molecule to form the sulfoxide. However, it is not unreasonable to suggest that with the sterically crowded sulfides **1a**–**c**, such a bimolecular reaction can become very difficult and the thiadioxirane (that probably is in a vibrationally excited state due to the very large exergonicity of its formation) may instead undergo C–S bond cleavage, presumably concerted with the opening of the three-member ring, leading to a quite stable tertiary carbocation and phenylsulfinate (Scheme 5, path b).[31] The phenylsulfinate should be oxidized to the sulfonate under the reaction conditions.[32] The alcohols (and alkenes) are formed from the carbocations as shown in Scheme 4. With **1a**, also *N*-*tert*-butylacetamide is formed,[33] whereas the alkene is not observed.



Scheme 5.

The formation of ketones **5**, that are a significant fraction of the products mixture obtained under air, may be justified by the possible reaction of the carbocation with $O_2^{-\bullet}$. An alkylperoxyl radical is formed that can be converted into ketone as shown in Scheme 6. Indeed, by generating the cumylperoxyl radical in the photolysis of cumene in the presence



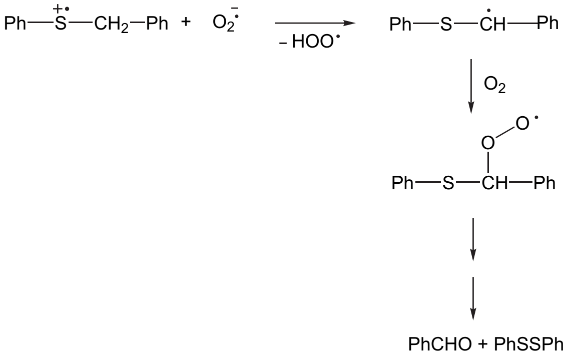
Scheme 6.

of di-*tert*-butyl peroxide and oxygen, benzophenone **5b** was obtained as the main product accompanied by small amounts of **3b** and **4b** (Section 5).[34]

3.2. Benzyl phenyl sulfide

The behaviors of sulfide (**2**) were similar to that of the *tert*-alkyl phenyl sulfides, discussed above. Thus, laser photolysis experiments showed the formation of the sulfide radical cation (in this case the dimeric form was also observed) that, however, decayed without the apparent formation of any transient. The decay rate followed second-order kinetics with a $k_2\varepsilon$ value very close to that found with the radical cations of *tert*-alkyl phenyl sulfides. In this case too the decay rate was faster under oxygen than under nitrogen (Table 3). As with *tert*-alkyl phenyl sulfides, steady-state photolysis of **2** sensitized by NMQ^+ led to significant amounts of products (benzyl phenyl sulfoxide and benzaldehyde) only in the presence of oxygen. However, when the photolysis was run in the presence of benzoquinone the yield of products dropped almost to zero in the presence of oxygen.

It seems clear that with **2**, the reaction of the sulfide radical cation with $O_2^{-\bullet}$ also plays a key role in product formation. When $O_2^{-\bullet}$ attacks sulfur, thiadioxirane forms leading to sulfoxide by reaction with another molecule of sulfide, as previously suggested for electron transfer sulfoxygenations.[15] In this case, the sulfide is not sterically congested, thus this reaction predominates with respect to the C–S bond cleavage reactions observed with **1a**–**c**.[35] However, since α-CH bonds are present in $\mathbf{2}^{+\bullet}$, $O_2^{-\bullet}$ can also perform a deprotonation process forming an α-phenylthio carbon radical that can lead to benzaldehyde and diphenyl disulfides by reaction with O_2, as shown in Scheme 7. The possibility that in electron transfer sulfoxygenations of sulfides with α-CH bonds, C–S bond cleavage products would derive from deprotonation of the sulfide radical cation had already been proposed,[13] but the key role played by $O_2^{-\bullet}$ in this respect had not been hitherto demonstrated.



Scheme 7.

4. Conclusions

The results of LFP and steady-state photolysis experiments have allowed us to reach the important conclusion that the C–S bond cleavage products formed in the photooxygenation of *tert*-alkyl phenyl sulfides sensitized by NMQ^+ mainly derive from the sterically congested thiadioxirane formed by the reaction of the sulfide radical cation with $O_2^{-\bullet}$. The mesolytic rupture of the C–S bond in the intermediate radical cation plays a minor role. A different situation holds with benzyl phenyl sulfide **2** (a primary alkyl sulfide with α-CH bonds) where the fragmentation product, benzaldehyde, is suggested to come from deprotonation of $\mathbf{2}^{\bullet+}$ by $O_2^{-\bullet}$ in competition with the formation of thiadioxirane. The latter species is much less congested than that formed from *tert*-alkyl phenyl sulfides and can therefore react, as expected, with another sulfide molecule to give benzyl phenyl sulfoxide that accordingly is among the reaction products.

5. Experimental

5.1. Starting materials

Commercial benzyl phenyl sulfide (**2**) was further purified by recrystallization from $EtOH/H_2O$. *tert*-Butyl phenyl sulfide (**1a**) was prepared by acid catalyzed reaction of thiophenol with *tert*-butanol.[36] 2-Phenyl-2-propyl phenyl sulfide (**1b**) and 1,1-diphenylethyl phenyl sulfide (**1c**) were prepared by acid catalyzed addition of thiophenol on α-methylstyrene and 1,1-diphenylethylene, respectively.[37] CH_3CN (spectrophotometric grade) and toluene were used as received. *N*-Methylquinolinium tetrafluoroborate was prepared according to a literature procedure.[38]

5.2. Quantum yields

A 2 ml solution of NMQ^+ (4×10^{-4} M) in CH_3CN and **1a**–**c** and **2** (1.0×10^{-2} M) in CH_3CN (CD_3CN in the case of **1a**) was placed in a quartz cuvette and irradiated at 313 nm, selected with a Balzer interference filter by a high pressure Hg lamp. The substrate conversion to photoproduct was held below 10% to avoid secondary reactions. The photoproducts were quantified by GC and ^1H NMR. Bibenzyl was used as an internal standard. The products from sulfide **1a** were analyzed exclusively by ^1H NMR, because of their high volatility. Water soluble photoproducts were identified by ^1H NMR after evaporation of the solvent CH_3CN and addition of D_2O. All products formed were identified by comparison with authentic specimens. *tert*-Butyl acetamide, acetophenone, benzophenone, 2-phenyl-2-propanol, α-methylstyrene, 1,1-diphenylethanol, 1,1-diphenylethylene, *tert*-butanol, acetone, benzaldehyde, diphenyl disulfide, sodium benzenesulfonate were commercial products. Benzyl phenyl sulfoxide was prepared by oxidation of benzyl phenyl sulfide with $NaIO_4$.[39] The light intensity (ca. 1×10^{15} photons s^{-1}) was measured by potassium ferric oxalate actinometry.[40]

5.3. Steady-state photooxidation of cumene

By irradiation of *tert*-butyl peroxide (0.16 M) at 313 nm in the presence of cumene (1.0×10^{-2} M) in O_2-saturated CH_3CN, acetophenone (3.4%), α-methylstyrene (1.0%), and 1,1-diphenylethanol (0.8%) formed after 7 h.

5.4. Fluorescence quenching

Measurements were carried out on a Spleg Fluorolog F112AF spectrofluorometer. Relative emission intensities at 390 nm (NMQ^+ emission maximum) were measured by irradiating at 315 nm (NMQ^+ absorption maximum) a solution containing NMQ^+ (1.0×10^{-5} M) and the substrates **1a–c** and **2** at different concentrations (from 0 to 7.0×10^{-3} M) in CH_3CN at 22 °C. The error estimated on the Stern–Volmer constants (K_{SV}) was ±5%.

5.5. Laser flash photolysis

The excitation wavelength of 355 nm from a Nd:YAG laser (Continuum, third harmonic) was used in nanosecond flash photolysis experiments (pulse width ca. 7 ns and energy <3 mJ per pulse). The transient spectra were obtained by a point-to-point technique, monitoring the absorbance changes (ΔA) after the flash at intervals of 5–10 nm over the spectral range 350–850 nm, averaging at least 10 decays at each wavelength. The lifetime values (the time at which the initial signal is reduced to $1/e$, experimental error ±10%) are reported for transients showing first-order decay kinetics. The k_2/ε values are reported for the transients showing second-order kinetics. A 2 ml solution containing the substrate (1.0×10^{-2} M), NMQ^+ (4×10^{-4} M) and the cosensitizer (1 M toluene) was flashed in a quartz photolysis cell while nitrogen or oxygen was bubbling through them. All measurements were carried out at 22±2 °C. The experimental error was ±10%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2005.09.154.

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30. The effect of benzoquinone also shows that the higher quantum yields in the presence of oxygen are not due to a suppression of the BET process by the reaction of $NMQ^\bullet$ with O_2. This possibility is also made unlikely by the fact that no transients were observed in the laser photolysis experiments in the presence of O_2.
31. Theoretical calculations (B3LYP/6-31G* level) have shown that such a C–S bond cleavage, in CH_3CN as solvent, is exothermic by 11 kcal mol^{-1}. We are very grateful to Dr. M. F. Gerini for performing this calculation.
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33. *tert*-Butyl cation is less stable and less selective than the cations from **1a** and **1b**, therefore it can also react with the solvent that is a weaker nucleophile than water.
34. It might be suggested that the C–S bond breaking in the thiadioxirane is homolytic forming a benzenesulfonyl radical and a carbon radical. Reaction of the carbon radical with oxygen should lead to the observed reaction products. However, the formation of *N-tert*-butylacetamide is a clear indication that a carbocation is also formed and supports the heterolytic

cleavage. Moreover, in this case the ketone would be the main reaction product, which is not observed.

35. In the photooxygenation of **2** sensitized by 9,10-dicyanoanthracene we have also observed the formation of benzyl derivatives.[17] However, those experiments were carried out at a significantly higher temperature, $\geq$40 °C.
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