Photosensitized Oxidation of Alkyl Phenyl Sulfoxides. C−S Bond Cleavage in Alkyl Phenyl Sulfoxide Radical Cations

Enrico Baciocchi,*,[§] Tiziana Del Giacco,*,[‡] Osvaldo Lanzalunga,*,[†] Paolo Mencarelli,*,[†] and Barbara Procacci[‡]

Dipartimento di Chimica and Istituto CNR di Metodologie Chimiche-IMC, Sezione Meccanismi di Reazione c/o Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, 00185 Rome, Italy, and Dipartimento di Chimica and Centro di Eccellenza Materiali Innovativi Nanostrutturati, Università di Perugia, via Elce di sotto 8, 06123 Perugia, Italy

osvaldo.lanzalunga@uniroma1.it

Received May 20, 2008
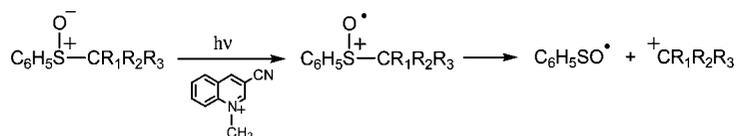
The 3-cyano-*N*-methylquinolinium perchlorate (3-CN-NMQ$^+$ ClO$_4^-$)-photosensitized oxidation of phenyl alkyl sulfoxides (PhSOCR$_1$R$_2$R$_3$, **1**, R$_1$ = R$_2$ = H, R$_3$ = Ph; **2**, R$_1$ = H, R$_2$ = Me, R$_3$ = Ph; **3**, R$_1$ = R$_2$ = Ph, R$_3$ = H; **4**, R$_1$ = R$_2$ = Me, R$_3$ = Ph; **5**, R$_1$ = R$_2$ = R$_3$ = Me) has been investigated by steady-state irradiation and nanosecond laser flash photolysis (LFP) under nitrogen in MeCN. Steady-state photolysis showed the formation of products deriving from the heterolytic C−S bond cleavage in the sulfoxide radical cations (alcohols, R$_1$R$_2$R$_3$COH, and acetamides, R$_1$R$_2$R$_3$CNHCOCH$_3$) accompanied by sulfur-containing products (phenyl benzenethiosulfinate, diphenyl disulfide, and phenyl benzenethiosulfonate). By laser irradiation, the formation of 3-CN-NMQ$^\bullet$ (λ_{max} = 390 nm) and sulfoxide radical cations **1**$^{\bullet+}$, **2**$^{\bullet+}$, and **5**$^{\bullet+}$ (λ_{max} = 550 nm) was observed within the laser pulse. The radical cations decayed by first-order kinetics with a process attributable to the heterolytic C−S bond cleavage leading to the sulfinyl radical and an alkyl carbocation. The radical cations **3**$^{\bullet+}$ and **4**$^{\bullet+}$ fragment too rapidly, decaying within the laser pulse. The absorption band of the cation Ph$_2$CH$^+$ (λ_{max} = 440 nm) was observed with **3** while the absorption bands of 3-CN-NMQ$^\bullet$ and PhSO$^\bullet$ (λ_{max} = 460 nm) were observed just after the laser pulse in the LFP experiment with **4**. No competitive β-C−H bond cleavage has been observed in the radical cations from **1**−**3**. The C−S bond cleavage rates were measured for **1**$^{\bullet+}$, **2**$^{\bullet+}$, and **5**$^{\bullet+}$. For **3**$^{\bullet+}$ and **4**$^{\bullet+}$, only a lower limit (ca. >3 × 10^7 s^{-1}) could be given. Quantum yields (Φ) and fragmentation first-order rate constants (k) appear to depend on the structure of the alkyl group and on the bond dissociation free energy (BDFE) of the C−S bond of the radical cations determined by a thermochemical cycle using the C−S BDEs for the neutral sulfoxides **1**−**5** obtained by DFT calculations. Namely, Φ and k increase as the C−S BDFE becomes more negative, that is in the order **1** < **5** < **2** < **3**, **4**, which is also the stability order of the alkyl carbocations formed in the cleavage. An estimate of the difference in the C−S bond cleavage rate between sulfoxide and sulfide radical cations was possible by comparing the fragmentation rate of **5**$^{\bullet+}$ (1.4 × 10^6 s^{-1}) with the upper limit (10^4 s^{-1}) given for *tert*-butyl phenyl sulfide radical cation (Baciocchi, E.; Del Giacco, T.; Gerini, M. F.; Lanzalunga, O. *Org. Lett.* **2006**, *8*, 641−644). It turns out that sulfoxide radical cations undergo C−S bond breaking at a rate at least 2 orders of magnitude faster than that of corresponding sulfide radical cations.

Introduction

Fragmentation of radical cations to form a cation and a radical (eq 1) is one of the most interesting reactions of these species which has attracted considerable attention for the theoretical implications as well as for the variety of possible applications (e.g., photography and polymerization initiations)[1] and the possible role in many biological and chemical oxidation processes.[2]

$$\overset{+\bullet}{A}\text{−B−C} \rightarrow \text{A−B}^\bullet + \text{C}^+ \qquad (1)$$

The feasibility of reaction (1) is due to the extra energy that in the radical cation is associated with the removal of an electron

[†] Sapienza Università di Roma.
[‡] Università di Perugia.
[§] IMC - Sapienza Università di Roma.

from the HOMO of the parent substrate (A−B−C). In most cases, the extra energy is predominantly located in the bond β to the center of positive charge as it is the one that can overlap most conveniently with the SOMO of the radical cation. The BDE of this bond significantly decreases, and therefore, the bond can be broken with relative ease. So one generally speaks of β fragmentations of radical cations. However, somewhat different situations can arise in alkyl aryl sulfide radical cations.[3] In this case, the positive charge is mainly located on the sulfur and the cleavage can involve the sulfur carbon bond (an α bond with respect to the positive charge) as shown in eq 2.

$$Ar\overset{+\bullet}{S}-CR_1R_2R_3 \rightarrow ArS^\bullet + {}^+CR_1R_2R_3 \qquad (2)$$
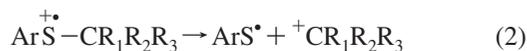
Our long-standing interest in the fragmentation reactions of radical cations has recently led us to focus our attention on the quantitative aspects of reaction (2) through a laser photolysis study.[4] The main observations were that the fragmentation rate depends to a very limited extent on the strength of the C−S bond in the radical cation and that the reorganization energy of the process was influenced by the structure of the alkyl groups, increasing with the number of phenyl groups bonded to the carbon atom.

Like sulfide radical cations, sulfoxide radical cations can also undergo fragmentation reactions (eq 3) involving the cleavage of the C−S bond. In fact, since sulfoxides are characterized by significantly higher oxidation potentials than that of the corresponding sulfides[5] and the phenylsulfinyl radical is more stable than the phenylthiyl radical,[8] reaction (3) is expected to be much faster than reaction (2). Thus, sulfoxide radical cations should represent an interesting class of radical cations characterized by a very high fragmentation rate.

$$Ar\overset{O^\bullet}{\underset{|}{S}}{}^+-CR_1R_2R_3 \longrightarrow ArSO^\bullet + {}^+CR_1R_2R_3 \qquad (3)$$
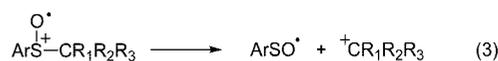
Aspects concerning generation, spectral properties, and structure of sulfoxide radical cations have been recently investigated in our laboratory,[6] but practically nothing is known about their fragmentation process with respect to both products and reactivity. Thus, we have felt it worthwhile to fill this gap, and we now report in this paper a steady state and laser photolysis study of the fragmentation reactions of a number of alkyl phenyl sulfoxide radical cations ($1^{\bullet+}-5^{\bullet+}$) generated by the photosensitized one-electron oxidation of alkyl phenyl sulfoxides **1−5** in MeCN.
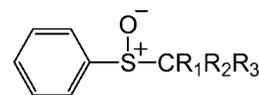
1 R$_1$ = Ph; R$_2$, R$_3$ = H
2 R$_1$ = Ph; R$_2$ = Me; R$_3$ = H
3 R$_1$, R$_2$ = Ph; R$_3$ = H
4 R$_1$ = Ph; R$_2$, R$_3$ = Me
5 R$_1$, R$_2$, R$_3$ = Me

Given the relatively high oxidation potential of sulfoxides ($\sim$2 V vs SCE),[6] 3-cyano-*N*-methylquinolinium perchlorate (3-CN-NMQ$^+$) was used as the sensitizer[9] (E° for 3-CN-NMQ^{+*}/3-CN-NMQ$^\bullet$ = 2.72 V vs SCE).[11] DFT calculations were also performed to obtain the values of bond dissociation energy (BDE) for the C−S bond in sulfoxides **1−5** and from them the values of the bond dissociation free energy (BDFE) in the corresponding radical cations.

Results

Quenching of Fluorescence. All the sulfoxides examined (**1−5**) efficiently quenched the fluorescence emission of 3-CN-NMQ$^+$ in accordance with the Stern−Volmer equation (4) where I_0 and I are the emission intensities in the absence and in the presence of increasing concentrations of sulfoxides ([Q]), respectively. The quenching rate constants (k_q) were calculated from the slopes of the linear Stern−Volmer plots (K_{SV}) divided by the lifetime of ^{1}3-CN-NMQ^{+*} measured in N$_2$-saturated CH$_3$CN (45 ns).[11] All the k_q values are very high and close to the diffusion limit ($1.1-1.5 \times 10^{10}$ M^{-1} s^{-1}). The efficient quenching process involves an electron-transfer from the sulfoxides to ^{1}3-CN-NMQ^{+*} as confirmed by laser flash photolysis experiments (see below) and in agreement with the reduction potential of ^{1}3-CN-NMQ^{+*}(2.72 V vs SCE in CH$_3$CN),[11] which is much higher than that of the sulfoxides examined (ca. 2.0 V vs SCE in CH$_3$CN).[6]

$$I_0/I = 1 + K_{SV}[Q] \qquad (4)$$

Steady-State Photolysis. Steady-state photolysis experiments were carried out by irradiating a solution of sulfoxides **1−5** (0.01 M) in N$_2$-saturated CD$_3$CN at around 355 nm in the presence of 3-CN-NMQ$^+$ ClO$_4^-$ (0.001 M). The amount of sulfoxide used was able to quench ca. 85% of the quinolinium singlet state. The products were identified and quantitated by ^{1}H NMR (products from the alkyl moiety) and HPLC (sulfur containing products) analysis by comparison with authentic specimens. No products were detected without irradiation or in the absence of the sensitizer. UV and ^{1}H NMR analysis of the reaction mixture after photolysis indicated that the sensitizer is not consumed during the irradiation.

(1) (a) Baciocchi, E.; Bietti, M.; Lanzalunga, O. *Acc. Chem. Res.* **2000**, *33*, 243. (b) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292. (c) Maslak, P. *Top. Curr. Chem.* **1993**, *168*, 1. (d) Albini, A.; Fasani, E.; d'Alessandro, N. *Coord. Chem. Rev.* **1993**, *125*, 269.

(2) (a) Filipiak, P.; Hug, G. L.; Carmichael, I.; Korzeniowska-Sobczuk, A.; Bobrowski, K.; Marciniak, B. *J. Phys. Chem. A* **2004**, *108*, 6503. (b) Huang, M. L.; Rauk, A. *J. Phys. Chem. A* **2004**, *108*, 6222. (c) Baciocchi, E.; Del Giacco, T.; Elisei, F.; Gerini, M. F.; Lapi, A.; Liberali, P.; Uzzoli, B. *J. Org. Chem.* **2004**, *69*, 8323. (c) Schöneich, C.; Pogocki, D.; Hug, G. L.; Bobrowski, K. *J. Am. Chem. Soc.* **2003**, *125*, 13700. (d) Korzeniowska-Sobczuk, A.; Hug, G. L.; Carmichael, I.; Bobrowski, K. *J. Phys. Chem. A* **2002**, *106*, 9251. (e) Gawandi, V. B.; Mohan, H.; Mittal, J. P. *J. Phys.Chem. A* **2000**, *104*, 11877. (f) Glass, R. S. *Top. Curr. Chem.* **1999**, *205*, 1.

(3) (a) Peñéñory, A. B.; Argüello, J. E.; Puiatti, M. *Eur. J. Org. Chem.* **2005**, *10*, 114. (b) Adam, W.; Argüello, J. E.; Peñéñory, A. B. *J. Org. Chem.* **1998**, *63*, 3905. (c) Ioele, M.; Steenken, S.; Baciocchi, E. *J. Phys. Chem. A* **1997**, *101*, 2979. (d) Baciocchi, E.; Lanzalunga, O.; Malandrucco, S.; Ioele, M.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 8973. (e) Baciocchi, E.; Rol, C.; Scamosci, E.; Sebastiani, G. V. *J. Org. Chem.* **1991**, *56*, 5498.

(4) Baciocchi, E.; Del Giacco, T.; Gerini, M. F.; Lanzalunga, O. *Org. Lett.* **2006**, *8*, 641–644.

(5) For example the peak potential of methyl phenyl sulfoxide in CH$_3$CN (2.01 V vs SCE)[6] is significantly higher than that of thioanisole (1.47 V vs SCE).[7]

(6) Baciocchi, E.; Del Giacco, T.; Gerini, M. F.; Lanzalunga, O. *J. Phys. Chem. A* **2006**, *110*, 9940–9948.

(7) Baciocchi, E.; Intini, D.; Piermattei, C.; Rol, C.; Ruzziconi, R. *Gazz. Chim. Ital.* **1989**, *119*, 649–652.

(8) Kice, J. L. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Chapter 24.

(9) 3-Cyano-*N*-methylquinolinium (3-CN-NMQ$^+$) was preferred to *N*-methylquinolinium (NMQ$^+$) because the absorption band of the reduced quinolinium radical NMQ$^\bullet$ (λ_{max} = 550 nm)[10] overlaps with the absorption bands of sulfoxide radical cations (vide infra).

(10) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669–4683.

(11) Kitaguchi, H.; Ohkubo, K.; Ogo, S.; Fukuzumi, S. *J. Phys. Chem. A* **2006**, *110*, 1718–1725.

SCHEME 1

1: R¹=Ph, R²=R³=H   **1a**   **1b**
2: R¹=Ph, R²=CH₃, R³=H   **2a**   **2b**
3: R¹= R₂=Ph, R³=H   **3a**   **3b**
4: R¹=Ph, R²=R³= CH₃   **4a**
5 R¹=R²=R³=CH₃   **5a**   **5b**

The photolysis of sulfoxides **1**, **2**, and **5** produced alcohols (benzyl, α-methylbenzyl, and *tert*-butyl alcohol, respectively) and acetamides (benzyl, α-methylbenzyl, and *tert*-butyl acetamide, respectively) as main reaction products from the alkyl fragments. With **3**, the main reaction product observed was diphenylmethanol, whereas 2-phenyl-2-propanol (with traces of α-methylstyrene) was formed in the photolysis of **4**. Small amounts of carbonyl derivatives (generally less than 10% of the total products) were also observed with primary and secondary alkyl phenyl sulfoxides **1**, **2**, and **3** (benzaldehyde, acetophenone, and benzophenone, respectively), which were attributed to partial photooxidation of the alcohols under the reaction conditions. Accordingly, the steady-state photolysis of sulfoxides **1** and **3** sensitized by 3-CN-NMQ⁺ in N₂-saturated CH₃CN at several irradiation times showed that benzyl alcohol (from **1**) and diphenyl methanol (from **3**) are progressively converted into benzaldehyde and benzophenone, respectively, as the reaction proceeds (for details, see the Supporting Information). For the products coming from the alkyl moiety, the material balance was very satisfactory (>90%) in all experiments.

The sulfur-containing products identified in all cases were as follows: phenyl benzenethiosulfinate (PhSOSPh), diphenyl disulfide (PhSSPh), and phenyl benzenethiosulfonate (PhSO₂SPh). Quantitative HPLC analysis showed that the photolysis of **3** produced, after 15 min of irradiation, PhSOSPh (0.5%, referred to the initial amount of substrate), PhSSPh (1.3%), and PhS(O)₂SPh (0.8%), together with diphenyl methanol (8.3%) and benzophenone (1.0%). The material balance for the sulfurated products is only around 60%, thus indicating that other unidentified sulfur-containing products are formed.

On the basis of the above results, the outcome of the steady-state photolysis of **1–5** sensitized by 3-CN-NMQ⁺ can be substantially described by Scheme 1.

Clearly, the carbocation formed by C–S bond cleavage in the intermediate radical cation (eq 3 and vide infra) is the precursor of alcohols and acetamides. The sulfur-containing products certainly derive from the phenylsulfinyl radical which forms together with the carbocation from the C–S bond scission (eq 3).

As a possible route to the sulfurated products, a possible suggestion, which will receive some support from the laser photolysis experiments (vide infra), is that the sulfinyl radical is first reduced to phenyl sulfenate by 3-CN-NMQ⁺ (eq 5).

$$3\text{-CN-NMQ}^\bullet + \text{PhSO}^\bullet \rightarrow 3\text{-CN-NMQ}^+ + \text{PhSO}^- \quad (5)$$

This reaction is thermodynamically feasible as the reduction potential of PhSO⁺ (1.08 V vs SCE in CH₃CN, calculated at 25 °C on the basis of a thermochemical cycle)[12] is much higher than that of 3-CN-NMQ⁺ (−0.60 V vs SCE in CH₃CN)[17] and should therefore be very fast (vide infra). Moreover, reaction

SCHEME 2

TABLE 1. Quantum Yields (Φ) of Some Photoproducts Formed in the 3-CN-NMQ⁺ ClO₄⁻ Photosensitized Oxidation of Alkyl Phenyl Sulfoxides (1–5) in N₂-Saturated CD₃CN[a]

sulfoxide	Φ(a)[b]	Φ(b)[c]	Φ_tot
1	0.089[d]	0.12	0.21
2	0.21[d]	0.21	0.42
3	0.66[d]		0.66
4	1.7		1.7
5	0.18	0.10	0.28

[a] [sulfoxide] = 1.0 × 10⁻² M, [3-CN-NMQ⁺ ClO₄⁻] = 1.0 × 10⁻³ M; quantum yields of the products from the alkyl moiety. [b] Quantum yields of alcohols, R₁R₂R₃COH. [c] Quantum yields of acetamides, R₁R₂R₃CNHCOCH₃. [d] The alcohol yield also includes the small amount of carbonyl compound formed by oxidation of the alcohol (see text). The actual Φ of the alcohol is therefore slightly higher than that in the table as photons have been also used to photoxidize the alcohol.

(5) would nicely explain the otherwise inexplicable observation that 3-CN-NMQ⁺ is not consumed during the irradiation.

The formation of the sulfenate anion may reasonably account for the sulfur-containing products formed in the steady-state photolysis. Accordingly, this species and/or its protonated form are characterized by a very rich chemistry and can promote a number of reactions[8](some are reported in Scheme 2) leading to PhSOSPh, PhSSPh, and PhSO₂SPh. Moreover, sulfinic acid can also be formed, which might get lost during workup, thus explaining the low overall quantum yield of sulfur-containing products as compared to that of the products from the alkyl moiety.

(12) $E°(\text{PhSO}^\bullet/\text{PhSO}^-) = \Delta G°(\text{PhSO-H})/23.06 + E°(\text{H}^\bullet/\text{H}^+) - 0.059\text{p}K_a$, where $\Delta G°(\text{PhSO-H})$ is the Gibbs energy for the homolytic fragmentation of the PhSO–H bond (78 kcal mol⁻¹), given by the PhSO–H bond dissociation energy (which can be assumed identical to that of CH₃SOH)[13] minus the entropy factor ($T\Delta S°$, taken as 8 kcal mol⁻¹ at 298 K),[14] $E°(\text{H}^+/\text{H}^\bullet)$ is the reduction potential of the proton (−2.0 V),[15] and pK_a is related to the dissociation of the phenyl sulfenic acid PhSOH (pK_a = 5).[16]
(13) Gollnick, K.; Strake, H.-U. *Pure Appl. Chem.* **1973**, *33*, 217–245.
(14) Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290–12295.
(15) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287–294.
(16) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 940–941.

SCHEME 3

The quantum yields (Φ) measured for the products (alcohols and acetamides) coming from the alkyl moiety of sulfoxides are reported in Table 1. Given the excellent material balance observed with these compounds, the sum of quantum yields of alcohols and acetamides (Φ_{tot}) also reported in Table 1 can be considered a measure of the photoefficiency of the fragmentation process.

An apparently intriguing observation is that **4** exhibits a quantum yield >1. This observation, however, can be reasonably explained by a thermal acid-catalyzed partial decomposition of the sulfoxide which occurs under the photolytic conditions. Accordingly, in the photolysis of **4**, protons are formed (deriving from the reaction of cumyl cation with adventitious water) which can be captured by the neutral sulfoxide. C—S bond cleavage in the protonated sulfoxide leads to the very stable cumyl cation and eventually to 2-phenyl-2-propanol (Scheme 3), thus apparently increasing the quantum yield.

In agreement with this explanation, we found that addition of $HClO_4$ (2.5×10^4 M) to a solution of **4** (0.01 M) in CD_3CN led, after 5 min, to the decomposition of 58% of sulfoxide with formation of cumyl alcohol (^1H NMR analysis) as the main product.[18]

Since the complication due to the acid catalyzed C—S cleavage in protonated sulfoxide should be related to the stability of the formed carbocation, the same experiment as above was also carried out with sulfoxide **3**, whose thermal decomposition should lead to a carbocation of stability similar to that of cumyl cation.[20] In this case, however, the substrate was recovered to a large extent (almost 90%) and only 10% of diphenyl methanol was formed. Thus, with **3**, the thermal decomposition should not significantly affect the quantum yield values in Table 1. Probably, the factor which makes **4** particularly susceptible to acid catalyzed C—S bond cleavage is the large steric hindrance in this tertiary system.[21] All the other sulfoxides examined were found stable under acidic conditions.

Laser Flash Photolysis Studies. The laser photolysis experiments ($\lambda_{exc} = 355$ nm) were performed under nitrogen in the presence of 1 M toluene as cosensitizer in order to increase the yields of radical cation.[25] Under these conditions, the couple $PhCH_3^{\bullet+}/3$-CN-NMQ$^\bullet$ is first formed, and it is $PhCH_3^{\bullet+}$ (E_{red} = 2.35 V vs SCE)[26] that converts the sulfoxide into the radical cation. The time-resolved spectra of sulfoxides **1**, **2**, and **5** were

very similar, whereas different features were observed in the time-resolved spectra of **3** and **4**. Upon laser excitation of the first three sulfoxides, two absorption bands were detected just after the laser pulse at 380−400 and 500−550 nm (Figure 1, where the time-resolved spectra of **5** are reported; those of **1** and **2** are in Figures S1 and S2 in the Supporting Information). Very likely, the absorption at around 390 nm is mostly due to 3-CN-NMQ$^\bullet$[27] and that at around 520 nm is due to the sulfoxide radical cation $5^{\bullet+}$.[6] The ΔA recorded at 520 nm within 30 μs (Figure 1, inset b) indicate a fast decay which should belong to the radical cation, followed by a slower decay which should be due to the radical PhSO$^\bullet$, that absorbs weakly at this wavelength (the absorption maximum is around 460 nm).[29]

At longer delay times (16 μs), the absorption at 390 nm is replaced by a residual absorption centered at 375 nm which decayed on a slower time scale (Figure 1, inset a) and might tentatively be attributed to the phenyl sulfenate formed according to eq 5.

As already mentioned, the time-resolved spectra obtained with **3** and **4** were different from those of **1**, **2**, and **5**. In the LFP experiments with 3-CN-NMQ$^+$/toluene/**3**, after the laser pulse only a large and intense band at about 440 nm was observed (Figure 2). This band can be assigned to the cation Ph_2CH^+ according to the literature.[30] The nature of this transient is confirmed by the fact that the decay of this absorption band (see Figure 2, inset) is not influenced by the presence of dioxygen.

The decay at 440 nm is very fast ($k = 3.2 \times 10^7$ s^{-1}) and is very likely due to the reaction of the carbocation with adventitious water,[31] responsible for the alcohol formation observed in the steady-state photolysis. Clearly, the fragmentation rate of the radical cation $3^{\bullet+}$ is so fast that the process takes place within the laser pulse. Thus, the radical cation is not observed, but only the carbocation produced in the fragmentation. The intense absorption band of Ph_2CH^+ ($\varepsilon \cong 50000$ M^{-1} cm^{-1})[30] overlaps and covers the less intense absorption bands of 3-CN-NMQ$^\bullet$ ($\varepsilon \cong 3500$ M^{-1} cm^{-1})[27] and PhSO$^\bullet$[29] fragments.

(17) Ohkubo, K.; Suga, K.; Morikawa, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 12850–12859.

(18) We also tried to carry out photolysis of **4** in the presence of pyridine which is a good base in CH_3CN.[19] However, this attempt failed because pyridine was a good quencher of the 3-CN-NMQ$^+$ excited state.

(19) Baciocchi, E.; Del Giacco, T.; Elisei, F.; Lapi, A. *J. Org. Chem.* **2006**, *71*, 853–860.

(20) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889.

(21) The steric hindrance in $3^{\bullet+}$, should be comparable or slightly lower than that in $5^{\bullet+}$ [E_s for CHPh$_2$ (−1.43)[22] is less negative than E_s for CMe$_3$ (−1.54)[23]]. Since the steric requirements of the methyl group are less than those of the phenyl group,[24] compound **4** should be characterized by the largest steric hindrance.

(22) Bowden, K.; Chapman, N. B.; Shorter, J. *J. Chem. Soc.* **1964**, 3370.

(23) Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(24) MacPhee, J. A.; Panaye, A.; Dubois, J.-E. *Tetrahedron* **1978**, *34*, 3553–3562. Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552–1556.

(25) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876–1883.

FIGURE 1. Time-resolved absorption spectra of the 3-CN-NMQ$^+$ (1.0 $\times$ 10^{-2} M)/toluene (1 M)/**5** (1.0 $\times$ 10^{-2} M) system in N$_2$-saturated CH$_3$CN recorded 0.32 ($\triangle$), 2 ($\blacktriangle$), 7.2 ($\bigcirc$) and ($\blacksquare$) 16 μs after the laser pulse (λ_{exc} = 355 nm). Inset: (a) decay kinetics recorded at 390 nm, (b) 520 nm.
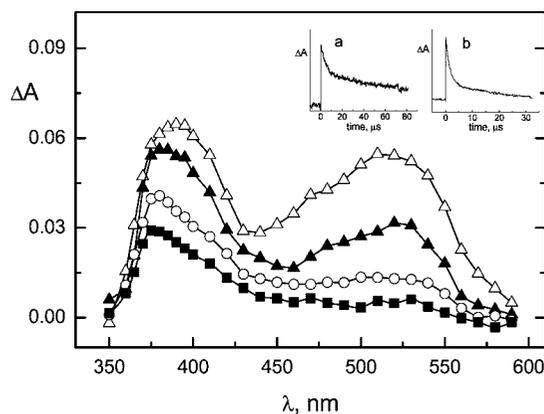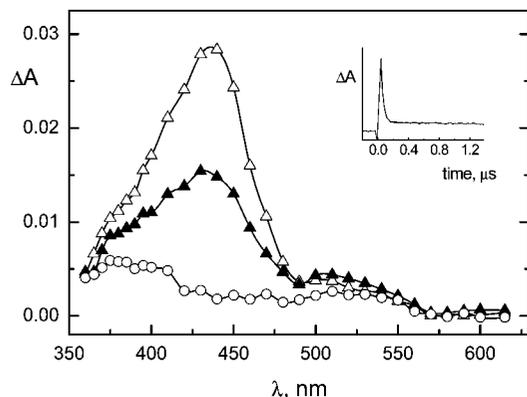
FIGURE 2. Time-resolved absorption spectra of the 3-CN-NMQ$^+$ (1.0 × 10^{-2} M)/toluene (1 M)/**3** (1.0 × 10^{-2} M) system in N$_2$-saturated CH$_3$CN recorded 0.040 (△), 0.064 (▲) and 3.2 (○) μs after the laser pulse (λ_{exc} = 355 nm). Inset: decay kinetics recorded at 440 nm.

A still different situation is found with the 3-CN-NMQ$^+$/ toluene/**4** system. In this case, too, the absorption band of **4**$^{•+}$ was not visible after the laser pulse, suggesting a very fast fragmentation. Thus, since the cumyl carbocation lifetime should be less than the limit of detection of the LFP apparatus,[32] the absorptions due to 3-CN-NMQ$^•$ (390 nm) and PhSO$^•$ (460 nm) can be clearly detected (Figure 3).

At longer delay times, a residual absorption was again observed at 380 nm which might tentatively be attributed to the phenyl sulfenate. The decay of the phenylsulfinyl radical follows second-order kinetics, with a rate constant of 1.9 × 10^{10} M^{-1} s^{-1} (see Figure S3 in the Supporting Information)[34] which is consistent with our previous suggestion that PhSO$^•$ decays by an electron transfer reaction with 3-CN-NMQ$^•$ (eq 5) to form the sensitizer 3-CN-NMQ$^+$ and the phenylsulfenate (PhSO$^-$). Some support for this hypothesis can be found in the observation that the half-life of PhSO$^•$ recorded at 470 nm (1.0 μs) is similar to that of 3-CN-NMQ$^•$ (1.2 μs) which has been determined from the initial fast decay of the absorption at 420 nm.[35] Moreover, the fact that the PhSO$^•$ decay is diffusion controlled (k = 1.9 ×

(26) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747–3756.

(27) The absorption spectrum of 3-CN-NMQ$^•$ (λ_{max} = 390 nm) was produced together with that of thioanisole (TA) radical cation (λ_{max} = 520 nm)[28] after laser flash photolysis of the 3-CN-NMQ$^+$/thioanisole/toluene system in CH$_3$CN. The extinction coefficient of 3-CN-NMQ$^•$ ($\varepsilon \cong$ 3500 M^{-1} cm^{-1}) was obtained from the following equation: ε_{390}(3-CN-NMQ$^•$) = ΔA_{390}(3-CN-NMQ$^•$) × ε_{520}(TA$^{•+}$)/ΔA_{520}(TA$^{•+}$), taking into account that the two transients 3-CN-NMQ$^•$ and TA$^{+•}$ have the same concentration and ε_{520}(TA$^{•+}$) = 6100 M^{-1} cm^{-1}.[28]

(28) Yokoi, H.; Hatta, A.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12728–12733.

(29) Darmanyan, A. P.; Gregory, D. D.; Guo, Y.; Jencks, W. S. *J. Phys. Chem. A* **1997**, *101*, 6855–6863.

(30) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918–6928.

(31) A lower value (2.5 × 10^6 s^{-1}) for the decay rate constant of the diphenylmethyl cation in CH$_3$CN, attributed to the reaction with water, is reported in the literature.[30] The difference is likely due to the higher water content in the CH$_3$CN used by us with respect to that used by Steenken et al. (ca. 0.01 M vs ≤0.002 M). Accordingly, when considering the second-order rate constants for the reaction of Ph$_2$CH$^+$ with water, we can estimate a value (3.2 × 10^9 M^{-1} s^{-1}) of the same order of magnitude as that determined by Steenken et al. ($k_2 \leq$ 1.3 × 10^9 M^{-1} s^{-1}).
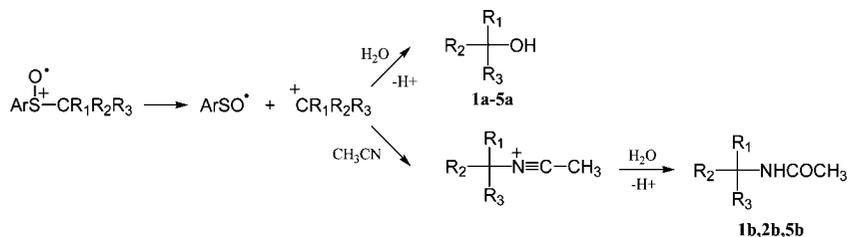
(32) The rate of decay of the cumyl cation in the low nucleophilic solvent 2,2,2-trifluoroethanol is >5 × 10^7 s^{-1}.[33]

(33) Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1999**, *77*, 2069–2082.

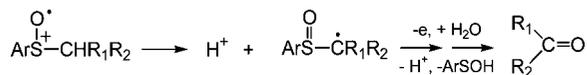(34) This value is not compatible with a self-recombination reaction (k = 3.0 × 10^9 M^{-1} s^{-1}).[29]

(35) This wavelength has been chosen to reduce the influence of the residual absorption.

FIGURE 3. Time-resolved absorption spectra of the 3-CN-NMQ$^+$ (8.8 × 10^{-4} M)/toluene (1 M)/**4** (1.0 × 10^{-2} M) system in N$_2$-saturated CH$_3$CN recorded 0.08 (△), 1.4 (▲), 6.3 (○) μs after the laser pulse. λ_{exc} = 355 nm.

TABLE 2. Total Quantum Yields (Φ) of Photoproducts Formed in the 3-CN-NMQ$^+$ ClO$_4^-$-Photosensitized Oxidation of Alkyl Phenyl Sulfoxides (1−5) and Decay Rate Constants of the Corresponding Radical Cations, C−S Bond Dissociation Energies (BDEs) for the Alkyl Phenyl Sulfoxides 1−5, and *tert*-Butyl Phenyl Sulfide and C−S Bond Dissociation Free Energies (BDFEs) For Their Corresponding Radical Cations

substrate	Φ_{tot}[a]	k (10^6 s^{-1})[b]	C−S BDE (neutral substrates)[c,d]	C−S BDFE (radical cations)[d,e,f]
1	0.21	1.1	29.9	−9.6
2	0.42	2.6	28.2	−19.6
3	0.66	>30	21.4	−27.0
4	1.7	>30	26.5	−26.2
5	0.28	1.4	36.2	−18.1
C$_6$H$_5$SC(CH$_3$)$_3$		<0.01[g]	53.6	7.6[h]

[a] In N$_2$-saturated CD$_3$CN. [sulfoxide] = 1.0 × 10^{-2} M, [3-CN-NMQ$^+$ ClO$_4^-$] = 1.0 × 10^{-3} M; quantum yields of the products from the alkyl moiety. [b] In N$_2$-saturated CH$_3$CN. [sulfoxide] = 1.0 × 10^{-2} M, [3-CN-NMQ$^+$ ClO$_4^-$] = 8.8 × 10^{-4} M, [toluene] = 1.0 M, [c] From DFT calculations, see text. [d] kcal mol^{-1}. [e] At 298 K. [f] Details of calculations in the Supporting Information. [g] From ref 4 using *N*-methoxy-phenanthridinium as sensitizer. [h] Reference 39.

10^{10} M^{-1} s^{-1}) may be considered consistent with the already mentioned very large exergonicity ($\Delta G° \cong$ −2 eV) of reaction (5).

The decay rates of the radical cations **1**$^{•+}$, **2**$^{•+}$, and **5**$^{•+}$ were determined in the presence of nitrogen by following the kinetics at 560 nm (Figure S4−S6 in the Supporting Information). This wavelength, higher than that corresponding to the λ_{max} of the radical cations, was chosen in order to reduce the overlap of the radical cation absorption with that of PhSO$^•$. In all cases, the decay kinetics followed first order laws, which shows that, given the high fragmentation rates, back-electron transfer is not a problem with sulfoxide radical cations, as previously reported for sulfide radical cations.[36] Thus, the C−S bond cleavage rates were conveniently measured for **1**$^{•+}$, **2**$^{•+}$, and **5**$^{•+}$. For **3**$^{•+}$ and **4**$^{•+}$, however, as already said, fragmentation rates were too fast for our apparatus (the radical cations were not observed) and only a lower limit (ca. >3 × 10^7 s^{-1}) could be given. The rate constants are reported in Table 2, along with the quantum yields (Φ_{tot}).

Theoretical Calculations. For a meaningful discussion of the experimental results, it was necessary to know the C−S

(36) Baciocchi, E.; Del Giacco, T.; Giombolini, P.; Lanzalunga, O. *Tetrahedron* **2006**, *62*, 6566–6573.

SCHEME 4

SCHEME 5

bond dissociation free energies (BDFEs) for the sulfoxide radical cations and, for the purpose of comparison, for the *tert*-butyl phenyl sulfide radical cation. These values were estimated by the usual thermochemical cycle[4] (details in the Supporting Information) using the C−S BDEs for the neutral counterparts (sulfoxides **1**−**5** and *tert*-butyl phenyl sulfide) obtained by DFT calculations, at the B3P86/6-311+G(d,p)//B3P86/6-311+G(d,p) level of theory. The B3P86 functional was chosen because it is reported to be applied with reasonable success to the calculation of BDE values for a variety of C−X bonds[37,38] including C−S bonds.[38] It should also be noted that even though DFT methods may underestimate absolute BDE values, this should not affect the relative BDE values[38c] which are those we are mostly concerned with in this paper. The calculated C−S BDEs of **1**−**5** and *tert*-butyl phenyl sulfide are reported in Table 2 together with BDFEs of the corresponding radical cations obtained by the thermochemical cycle. Further details of the calculations are given in the Experimental Section.

Discussion

The results of the steady-state photolysis experiments have clearly indicated that in all cases alcohols and (in the oxidation of **1**, **2**, and **5**) acetamides are formed, by far, as the major primary reaction products. Clearly, as also confirmed by laser photolysis, an alkyl cation is formed by C−S bond cleavage in the radical cation, which reacts with the solvent and (or) adventitious water to form the corresponding acetamide and alcohol, respectively (Scheme 4).

Formation of small amounts of carbonyl derivatives, benzaldehyde with **1** and ketones with **2** and **3**, was also observed. These products have been attributed (see the Results) to partial oxidation of the alcohol under the reaction conditions. It might also be suggested that the carbonyl compounds come, at least in part, from oxidation followed by reaction with adventitious water of the α-sulfoxyphenyl carbon radical formed by a competitive α-C−H bond cleavage in the radical cation (Scheme 5). However, this possibility is unlikely, particularly with **2** and **3**, as the lowest yield of carbonyl product is found with the sulfoxide **1** which is the one where the competition by α-C−H bond cleavage is expected to be more favored (vide infra). Thus,

it can be confidently concluded that C−S bond cleavage is the almost exclusive fragmentation process even when a deprotonation pathway (Scheme 5) might take place.

Interestingly, sulfoxide radical cations behave quite differently from the radical cations of the corresponding sulfides where β-C−H bond cleavage competes quite efficiently with C−S bond cleavage.[3,36] This outcome is certainly due to the fact that the breaking of the C−S bond is much easier in the sulfoxide than in the sulfide radical cations due to the already mentioned much higher stability of the phenylsulfinyl than phenylthiyl radicals.[8]

Looking at the problem in a more quantitative way, however, calculations based on the usual thermochemical cycle (details in the Supporting Information) show that in the benzyl phenyl sulfoxide radical cation, β-deprotonation still appears slightly more exergonic (about 2 kcal mol^{-1}) than the C−S bond cleavage path (BDFEs, −11.4 and − 9.6 kcal mol^{-1}, respectively). Probably, stereoelectronic factors which may unfavorably affect the deprotonation process are in play. Another hypothesis is that the reorganization energy for the deprotonation (β-cleavage) may be larger than for the breaking of the C−S bond (α cleavage). This is an important point which should deserve future attention from a theoretical point of view. For the sulfoxide radical cations **2**$^{•+}$ and **3**$^{•+}$ leading to a carbocation more stable than the benzyl cation,[40] C−S bond cleavage is always much more exergonic than deprotonation.

Both the Φ_{tot} and the k values, reported in Table 2, increase in the order **1** < **5** < **2** < **3**, **4**; i.e., they increase as the stability of the carbocation formed increases[40] and the BDFE of the scissile C−S bond in the sulfoxide radical cation (last column in Table 2) becomes more negative. It can also be noted that fragmentation rates parallel quantum yields almost quantitatively. Indeed, the reactivity ratios $k(\mathbf{2}^{+•})/k(\mathbf{1}^{+•}) = 2.4$, $k(\mathbf{5}^{•+})/k(\mathbf{1}^{+•}) = 1.3$ and $k(\mathbf{2}^{•+})/k(\mathbf{5}^{•+}) = 1.9$ are very similar to the quantum yields ratios, $\Phi(\mathbf{2})/\Phi(\mathbf{1}) = 2.0$, $\Phi(\mathbf{5})/\Phi(\mathbf{1}) = 1.3$ and $\Phi(\mathbf{2})/\Phi(\mathbf{5}) = 1.5$, respectively. An intriguing observation, however, is that quantum yields, as well as fragmentation rates, are very similar for **1**$^{•+}$ and **5**$^{•+}$, in spite of the large difference in driving force (8.5 kcal mol^{-1}) between the two fragmentation processes. Thus, it seems that the fragmentation rate of **1**$^{•+}$ is significantly larger than that expected on the basis of the BDFE of the C−S bond. At present, the most plausible hypothesis is that the C−S bond cleavage in **1**$^{•+}$ involving a primary carbon may benefit of nucleophilic assistance by the solvent or adventitious water. Such assistance is of course impossible with **5**$^{•+}$ whose C−S bond involves a nucleophilically inaccessible tertiary carbon.[41] Further work to check this suggestion might be of interest.

(37) (a) Yao, X.-Q.; Hou, X.-J.; Jiao, H.; Wu, G.-S.; Xu, Y.-Y.; Xiang, H.-W.; Jiao, H.; Li, Y.-W. *J. Phys. Chem. A* **2002**, *106*, 7184. (b) Zhao, J.; Cheng, X.; Yang, X. *THEOCHEM* **2006**, *766*, 87. (c) Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *ChemPhysChem* **2006**, *7*, 2205. (d) Su, X.-F.; Cheng, X.; Liu, Y.-G.; Li, Q. *Int. J. Quantum Chem.* **2007**, *107*, 515.

(38) (a) Johnson, E. R.; Clarkin, O. J.; DiLabio, G. A. *J. Phys. Chem. A* **2003**, *107*, 9953. (b) Yao, X.-Q.; Hou, X.-J.; Jiao, H.; Xiang, H.-W.; Li, Y.-W. *J. Phys. Chem. A* **2003**, *107*, 9991. (c) Feng, Y.; Liu, L.; Wang, J.-T.; Huang, H.; Guo, Q.-X. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 2005.

(39) Present work. In a previous paper,[4] we have reported a value of 10.7 kcal mol^{-1} for the C−S BDFE, based on a C−S BDE of 56.7 kcal mol^{-1} for *tert*-butyl phenyl sulfide, calculated by a different method.

(40) Abboud, J.-L. M.; Alkorta, I.; Davalos, J. Z.; Müller, P.; Quintanilla, E.; Rossier, J.-C. *J. Org. Chem.* **2003**, *68*, 3786–3796.

A precise comparison between the fragmentation (C−S bond cleavage) rates of sulfoxide and sulfide radical cations would have been of great interest, but this is not possible as the fragmentation rate of the sulfoxide radical cation **4**$^{•+}$ which might be compared with that known of the corresponding sulfide radical cation[4] was too fast to be measured. However, we can estimate that sulfoxide radical cations should fragment at least 2 orders of magnitude faster than sulfide radical cations. This consideration is based on the comparison of the fragmentation rate of *t*-butyl phenyl sulfoxide radical cation (**5**$^{•+}$) (1.4 × 10^6 M$^{−1}$ s$^{−1}$) with that of *tert*-butyl phenyl sulfide radical cation which has been estimated as <10^4 M$^{−1}$ s$^{−1}$,[4] (Table 2). Even though this difference may seem very large, it should be noted that it is associated with a really large change (almost 25 kcal mol$^{−1}$) in the C−S BDFE for the two radical cations, from 7.6 kcal mol$^{−1}$ for the sulfide to −18.1 kcal mol$^{−1}$ for the sulfoxide (Table 2).[42] Thus, the difference in fragmentation rate between sulfide and sulfoxide radical cations appears small relative to the difference in the thermodynamic driving force. This observation would suggest a reorganization energy for the fragmentation process significantly larger for sulfoxide than for sulfide radical cations. This might not be surprising since in the sulfoxide radical cation there is a very polar S−O bond, presumably well solvated in the polar MeCN, whose polarity and length change during the fragmentation process leading to the sulfinyl radical. Accordingly, the negative charge on oxygen is larger in the phenylsulfinyl radical[29] than in the methyl phenyl sulfoxide radical cation[6] and the opposite occurs with respect to the positive charge on sulfur. Moreover, comparing B3LYP calculations, the S−O bond length is 0.04 Å shorter in the sulfoxide radical cation than in the sulfinyl radical. Thus, both the internal and the solvent reorganization energies might be quite large.

Experimental Section

Materials. Benzyl phenyl sulfoxide (**1**), 1-phenylethyl phenyl sulfoxide (**2**), diphenylmethyl phenyl sulfoxide (**3**), 2-phenyl-2-propyl phenyl sulfoxide (**4**), and *tert*-butyl phenyl sulfoxide (**5**) were prepared by oxidation of the corresponding sulfides with sodium periodate in aqueous ethanol.[43] Benzyl phenyl sulfide is commercially available. 1-Phenylethyl phenyl sulfide, diphenylmethyl phenyl sulfide, and *tert*-butyl phenyl sulfide were prepared by acid-catalyzed reaction of thiophenol with 1-phenylethanol, diphenyl-methanol, and *tert*-butanol, respectively,[44] and 2-phenyl-2-propyl phenyl sulfide was prepared by acid-catalyzed addition of thiophenol on α-methylstyrene.[45] 3-Cyano-*N*-methylquinolinium perchlorate was prepared by reaction of 3-cyanoquinoline with dimethyl sulfate; the sulfate salt was then transformed to the perchlorate salt by using perchloric acid.[46] Alcohols **1a**−**5a**, carbonyl products (benzaldehyde, acetophenone, and benzophenone), and diphenyl disulfide are commercially available. Acetamides **1b**, **2b**, and **5b** and phenyl benzenethiosulfonate were prepared according to literature procedures.[3e,47,48] Phenyl benzenethiosulfinate was prepared

by oxidation of PhSSPh with the H$_2$O$_2$/MoO$_2$Cl$_2$ system in CH$_3$CN at room temperature.[49] Acetonitrile (spectrophotometric grade) was used as received.

Laser Flash Photolysis. Excitation wavelength of 355 nm (Nd: YAG laser, Continuum, third harmonic, pulse width ca. 7 ns and energy <3 mJ per pulse) was used in nanosecond flash photolysis experiments.[50] A 1 mL solution containing the substrate (1.0 × 10$^{−2}$ M), the sensitizer (3-CN-NMQ$^+$ClO$_4^−$, 8.8 × 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 transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (Δ*A*) after the laser flash at intervals of 5−10 nm over the spectral range 320−650 nm, averaging at least 10 decays at each wavelength. The error estimated on the rate constants was ±10%.

Fluorescence Quenching. Measurements were carried out on a Spex Fluorolog F112AF spectrofluorometer. Relative emission intensities at 427 nm (3-CN-NMQ$^+$ClO$_4^−$ emission maximum) were measured irradiating at 329 nm (3-CN-NMQ$^+$ClO$_4^−$ absorption maximum) a solution containing the sensitizer (<1.7 × 10$^{−5}$ M) with the substrate at different concentrations (from 9 × 10$^{−3}$ to 1 × 10$^{−2}$ M) in air-saturated CH$_2$Cl$_2$. The error estimated on the Stern−Volmer constants (K_{SV}) was ± 5%.

Quantum Yields. A 1 mL solution of 3-CN-NMQ$^+$ClO$_4^−$ (1.0 × 10$^{−3}$ M) and **1**−**5** (1.0 × 10$^{−2}$ M) in N$_2$-saturated CD$_3$CN was placed in a quartz cell and irradiated with four phosphor-coated fluorescent lamps emitting at 355 ± 15 nm. The light intensity (ca. 1 × 10^{15} photons s$^{−1}$) was measured by potassium ferric oxalate actinometry. The error estimated on the Φ values was ±10%. The photoproducts not containing sulfur were quantified by ^{1}H NMR analysis, by use of 1,4-dimethoxybenzene as internal standard. Phenyl benzenethiosulfinate (PhSOSPh), diphenyl disulfide (Ph-SSPh), and phenyl benzenethiosulfonate (PhSO$_2$SPh) were identified in the reaction of 3-CN-NMQ$^+$ (1.0 × 10$^{−3}$ M) and **3** (1.0 × 10$^{−2}$ M) in N$_2$-saturated CH$_3$CN (1 mL) after 15 min of irradiation. The photolyzed mixture was analyzed with HPLC by comparison with authentic specimens and quantitatively determined by using the direct calibration method.

Computational Details. All of the calculations were carried out by using the Gaussian 03 package.[51] Since we are dealing with conformationally flexible molecules, before starting the BDEs calculations, all of the available conformations for the molecule and the radicals formed in the C−S scission process have to be found. To this end, a systematic conformational search was carried out, at the semiempirical PM3 level of theory,[52] by using the Conformer Search Module available in the Spartan 5.01 package.[53] All of the conformers found were optimized again, first at the

(41) Probably no nucleophilic assistance takes place also with **3**$^{•+}$ and **4**$^{•+}$ involving C−S bonds with secondary carbons.

(42) This difference is in part due to the difference in oxidation potential between sulfoxide and sulfide (ca. 0.5 V higher for sulfoxide).[5] The rest (ca. 16 kcal mol$^{−1}$) can be associated with the higher stability of sulfinyl than sulfenyl radicals.

(43) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282−284.

(44) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1977**, *42*, 1462. Cutress, N. C.; Grindley, T. B.; Katritzky, A. R.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 263.

(45) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1979**, *44*, 713.

(46) Kato, S.; Nakata, J.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1928−1933.

(47) Lopez-Serrano, P.; Jongejan, J. A.; van Rantwijk, F.; Sheldon, R. A. *Tetrahedron: Asymmetry* **2001**, *12*, 219−228. Newcomb, M.; Varck, T. R.; Goh, S.-H. *J. Am. Chem. Soc.* **1990**, *112*, 5186.

(48) Kice, J. L.; Rogers, T. E. *J. Am. Chem. Soc.* **1974**, *96*, 8015−8019.

(49) Jeyakumar, K.; Chand, D. K. *Tetrahedron Lett.* **2006**, *47*, 4573−4576.

(50) Romani, A.; Elisei, F.; Masetti, F.; Favaro, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2147−2154. Görner, H.; Elisei, F.; Aloisi, G. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 29−34.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida M.; Nakajima, T.; Honda, Y.; Kitao O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*, Gaussian, Inc.: Pittsburgh, PA, 2003.

(52) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

B3LYP/6-31G level of theory and then at the higher B3P86/6-311+G(d,p) level of theory. The number of conformers found for sulfoxides **1**−**5** were: two for **1**, three for **2**, four for **3**, three for **4**, and one for **5**. Only one conformer was found for *t*ert-butyl phenyl sulfide and for each radical fragment.

In all of the calculations, the keywords integral(grid=Ultrafine) scf=tight were used. For open shell (radical) species, spin contamination due to states of multiplicity higher than the doublet state, was negligible since the expectation value $<S^2>$ of the total spin operator S^2 was, in all cases, within 5% of the expectation value for a doublet (0.75). Harmonic vibrational frequencies were calculated at the B3P86/6-311+G(d,p) level of theory to confirm that the stationary points found correspond to local minima and to obtain the zero-point vibrational energy (ZPVE) corrections. For the ZPVE a scale factor of 0.9845 was used.[54] When more than one conformer was found for a given compound, its energy ($E_{el} + E_{ZPVE}$) to be used in the BDEs calculation was obtained by Boltzmann averaging the energy ($E_{el} + E_{ZPVE}$) of all the corre-

sponding minima. In the Supporting Information are reported the Cartesian coordinates, the electronic energy, and the zero-point vibrational energy of all the minima found.

Supporting Information Available: Stability of photoproducts in the steady-state photolysis of the 3-CN-NMQ$^+$/**1** and 3-CN-NMQ$^+$/**3** systems, laser flash photolysis of the 3-CN-NMQ$^+$/toluene/**1** and 3-CN-NMQ$^+$/toluene/**2** systems, decay kinetics of PhSO$^{\bullet}$ at 470 nm, decay kinetics of **1**$^{+\bullet}$, **2**$^{+\bullet}$, and **5**$^{+\bullet}$ at 560 nm, C−S BDFEs for the sulfoxide and sulfide radical cations, C−H BDFE for benzyl phenyl sulfoxide radical cation, Cartesian coordinates, electronic energies, and zero-point vibrational energies obtained from DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801088N

(53) Spartan 5.01, Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

(54) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683.