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Photosensitized Oxidation of Aryl Benzyl Sulfoxides. Evidence for Nucleophilic Assistance to the C−S Bond Cleavage of Aryl Benzyl Sulfoxide Radical Cations

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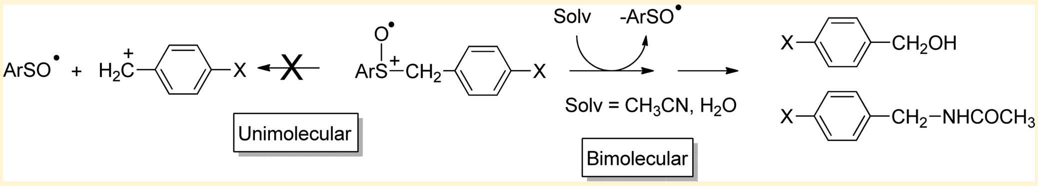
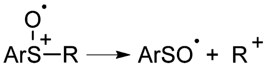
Ⓢ *Supporting Information*



ABSTRACT: The radical cations of a series of aryl benzyl sulfoxides ($4\text{-X-}C_6H_4CH_2SOC_6H_4Y^{+\bullet}$) have been generated by photochemical oxidation of the parent sulfoxides sensitized by 3-cyano-*N*-methylquinolinium perchlorate (3-CN-NMQ$^+ClO_4^-$). Steady-state photolysis experiments showed the prevailing formation of benzylic products deriving from the C−S fragmentation in the radical cations, together with sulfur-containing products. Formation of sulfoxide radical cations was unequivocally established by laser flash photolysis experiments showing the absorption bands of 3-CN-NMQ$^\bullet$ (λ_{max} = 390 nm) and of the radical cations (λ_{max} = 500−620 nm). The decay rate constants of radical cations, determined by LFP experiments, decrease by increasing the electron-donating power of the arylsulfinyl Y substituent and to a smaller extent by increasing the electron-withdrawing power of the benzylic X substituent. A solvent nucleophilic assistance to the C−S bond cleavage has been suggested, supported by the comparison of substituent effects on the same process occurring in aryl *tert*-butyl sulfoxide radical cations. DFT calculations, performed to determine the bond dissociation free energy in the radical cations, the transition state energies associated with the unimolecular C−S bond cleavage, and the charge and spin delocalized on their structures, were also useful to endorse the nucleophilic assistance to the C−S scission.

■ INTRODUCTION

The analysis of the reactivity and properties of sulfoxides has attracted the interest of several research groups in the past decades. This special interest is associated with the great number of synthetic organic procedures and important biological processes involving the sulfoxide functional group.[1,2] Notwithstanding, only a limited number of studies have been focused on the reactive species formed after one-electron oxidation of sulfoxides, i.e., the sulfoxide radical cations.[3] These studies have been hampered by the relatively high oxidation potentials of sulfoxides, which are significantly higher than those of the more easily oxidizable sulfides.[4] As a consequence, several aspects concerning the reactivity and properties of the sulfoxide radical cations have yet to be investigated. In this context, we have recently analyzed the heterolytic α-C−S bond fragmentation processes of aromatic sulfoxide radical cations, generated by photosensitized oxidation. This process leads to the formation of an arylsulfinyl radical, ArSO$^\bullet$, and an alkyl carbocation, R$^+$ (eq 1).[5−7]



$$ArS^{+}(O^{\bullet})\text{−}R \longrightarrow ArSO^{\bullet} + R^{+} \qquad (1)$$

In particular we analyzed the quantitative aspects of the C−S bond cleavage in alkyl phenyl sulfoxide radical cations and aryl *tert*-butyl sulfoxide radical cations produced by one-electron oxidation of the corresponding sulfoxides sensitized by 3-cyano-*N*-methylquinolinium (3-CN-NMQ$^+$).[6,7] With all the sulfoxides investigated, it was found that the C−S bond cleavage occurs with a fast first-order process ($k_d > 1.9 \times 10^5$ s^{-1}). A significant variation of the C−S fragmentation rate constants was observed by changing the structure of the alkyl group in alkyl phenyl sulfoxide radical cations, as expected on the basis of the different stability of the R$^+$ carbocations formed.[6] On the contrary, the electronic effect of aryl ring substituents on the fragmentation rate constants of aryl *tert*-butyl sulfoxide radical cations was not particularly remarkable.[7] This result has been attributed to the significant delocalization of charge and spin density on the *tert*-butyl group in the radical cations that reduces the importance of electronic effect of the aryl substituent on the C−S bond cleavage.

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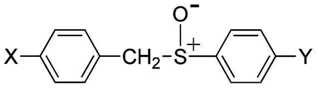
Along this line, to gain a comprehensive analysis of the substituent effects on the reactivity of aryl sulfoxide radical cations and to investigate the possible competition of solvent nucleophilic assistance to the C–S fragmentation, we have carried out a steady-state and laser flash photolysis study of the oxidation of aryl benzyl sulfoxides (**1**–**7**) photosensitized with 3-cyano-*N*-methylquinolinium perchlorate (3-CN-$\text{NMQ}^+\text{ClO}_4^-$). Sulfoxides **1**–**7** contain both electron-donating (ED) and electron-withdrawing (EW) substituents on either the benzylic or the arylsulfinyl rings. The singlet excited state of the sensitizer (3-CN-NMQ^{+*}) is characterized by a reduction potential ($E°$ = 2.72 V vs SCE)[8] much higher than that of the aryl benzyl sulfoxides investigated.[3]



1 X=Me, Y=H
2 X=H, Y=H
3 X=Cl, Y=H
4 X=CN, Y=H
5 X=H, Y=MeO
6 X=H, Y=Me
7 X=H, Y=Br

DFT calculations have been carried out to obtain the C–S bond dissociation energy values (BDEs) needed for the evaluation of the bond dissociation free energies (BDFEs) in the radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{7}^{+\bullet}$. DFT calculations have been also carried out to establish how the charge and the spin are delocalized between the two rings of the radical cations and of the transition states involved in the C–S bond cleavage process.

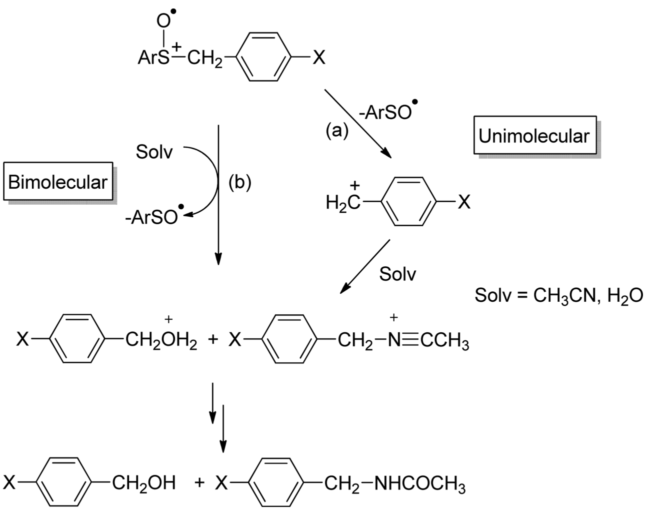
■ RESULTS

Steady-State Photolysis. Irradiation at 355 nm of solutions of aryl benzyl sulfoxides **1**–**7** (1.0×10^{-2} M) and 3-CN-$\text{NMQ}^+\text{ClO}_4^-$ (1.0×10^{-3} M) in CD_3CN under nitrogen led to the formation of the fragmentation products listed in Scheme 1. 4-X-Benzyl alcohols and 4-X-benzyl acetamides, identified by ^{1}H NMR analysis, were the main reaction products from the benzyl fragments, accompanied by smaller amounts of 4-X-benzaldehydes (≤1%). Diaryl disulfide (ArSSAr), aryl arenethiosulfinate (ArSOSAr), and aryl arenethiosulfonate (ArSO_2SAr) were identified by HPLC analysis as sulfurated fragmentation products.

The yields of benzylic fragmentation products, determined by ^{1}H NMR and referred to the initial amount of substrate, are reported in Table 1. The material balance (unreacted substrate plus benzylic products) was very satisfactory (>90%) in all experiments.

4-X-Benzyl acetamides and 4-X-benzyl alcohols could be produced from the 4-X-benzyl carbocations, formed after unimolecular C–S bond cleavage of 4-X-$\text{C}_6\text{H}_4\text{CH}_2\text{SOC}_6\text{H}_4\text{Y}^{+\bullet}$, by reaction with CH_3CN (Ritter reaction) or adventitious water (Scheme 2, path a), respectively.[5,9] However, another possible pathway involving a solvent nucleophilic assistance of C–S bond cleavage might be possible (Scheme 2, path b), as already suggested for $\mathbf{2}^{+\bullet}$[6] (see Discussion). The small amounts of 4-X-benzaldehydes are likely formed by further oxidation of the primary benzylic products under the reaction conditions.[6]

Scheme 2



The fact that the total yields of benzylic fragmentation products exceed the amount of sensitizer (10 mol % with respect to the substrate) indicates that the latter species is partially regenerated during the photolysis. As already observed in previous works,[6,7] UV–vis and ^{1}H NMR analysis showed that the amount of 3-CN-NMQ^+ consumed after photolysis was less than 20%. A possible path to regenerate 3-CN-NMQ^+ could be the exergonic oxidation reaction of 3-CN-$\text{NMQ}^\bullet$ by the sulfinyl radicals $\text{ArSO}^\bullet$ (eq 2).[10]

$$\begin{aligned}&3\text{-CN-NMQ}^\bullet + 4\text{-XC}_6\text{H}_4\text{SO}^\bullet\\ &\quad\rightarrow 3\text{-CN-NMQ}^+ + 4\text{-XC}_6\text{H}_4\text{SO}^- \qquad (2)\end{aligned}$$

The reaction sequence that leads to the formation of sulfur-containing products ArSSAr, ArSOSAr, and ArSO_2SAr has been previously described in the oxidation of aryl *tert*-butyl sulfoxide sensitized by 3-CN-NMQ^+.[7] ArSO_2SAr are formed by dimerization of $\text{ArSO}^\bullet$.[5,12] ArSSAr and ArSOSAr might be formed from the sulfenate anion, deriving from reduction of $\text{ArSO}^\bullet$, or from the sulfenic acid ArSOH, according to the reactions reported in Scheme 3.

Laser Flash Photolysis Studies. Upon laser excitation (λ_{exc} = 355 nm) of N_2-purged CH_3CN solutions of 3-CN-NMQ^+ (7×10^{-4} M) in the presence of sulfoxide (**1**–**7**, 1.0 ×

Scheme 1

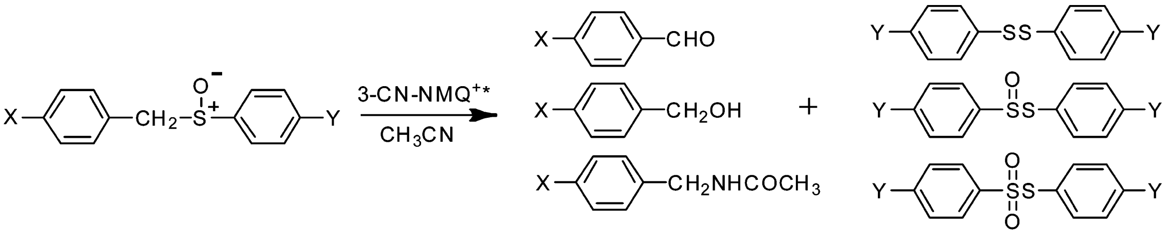
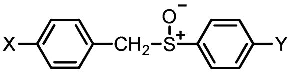
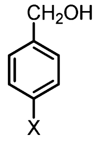
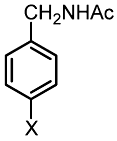
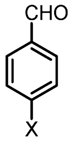
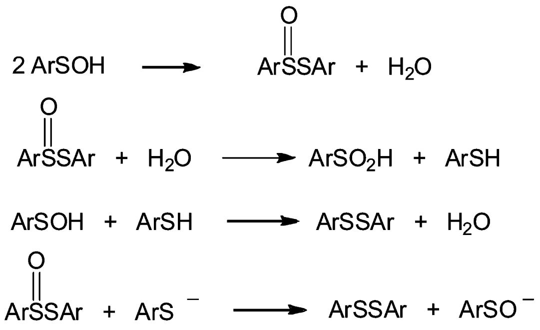


Table 1. Benzylic Products and Yields in the Oxidation of Aryl Benzyl Sulfoxides (1−7) Photosensitized by 3-CN-NMQ$^+$ in N$_2$-Saturated CD$_3$CN[a]

	Products (Yields %)[b]			
				Total benzylic products
1 X = CH$_3$, Y = H	4.8	12.5	0.2	17.5
2 X = Y = H	2.1	12.1	0.8	15
3 X = Cl, Y = H	1.0	12.8	1.0	14.8
4 X = CN, Y = H	5.6	2.0	0.9	8.5
5 X = H, Y = OCH$_3$	0.8	5.0	0.2	6
6 X = H, Y = CH$_3$	2.4	5.8	0.1	8.3
7 X = H, Y = Br	2.9	13.5	0.5	16.9

[a][Sulfoxide] = 1.0×10^{-2} M, [3-CN-NMQ$^+$ClO$_4^-$] = 1.0×10^{-3} M. [b]Yields refer to the initial amounts of substrate. The error is ±5%.

Scheme 3



$$2\,\mathrm{ArSOH} \longrightarrow \mathrm{Ar}\overset{O}{\overset{\|}{S}}\mathrm{SAr} + \mathrm{H_2O}$$

$$\mathrm{Ar}\overset{O}{\overset{\|}{S}}\mathrm{SAr} + \mathrm{H_2O} \longrightarrow \mathrm{ArSO_2H} + \mathrm{ArSH}$$

$$\mathrm{ArSOH} + \mathrm{ArSH} \longrightarrow \mathrm{ArSSAr} + \mathrm{H_2O}$$

$$\mathrm{Ar}\overset{O}{\overset{\|}{S}}\mathrm{SAr} + \mathrm{ArS}^- \longrightarrow \mathrm{ArSSAr} + \mathrm{ArSO}^-$$

10^{-2} M) and toluene as cosensitizer (1 M), time-resolved absorption spectra and decay kinetics were recorded. The radical cation PhCH$_3^{+\bullet}$, initially formed by electron transfer from the cosensitizer to the singlet excited-state 3-CN-NMQ^{+*}, is able to oxidize the sulfoxides to the corresponding radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ (E_{red} PhCH$_3^{+\bullet}$ = 2.35 V vs SCE).[13] The use of the cosensitizer reduces the efficiency of the back-electron-transfer process, leading to increased yields of sulfoxide radical cations.[14]

The time-resolved spectra recorded in the laser flash photolysis (LFP) experiments of sulfoxides **1**−**7** were very similar. As examples, in Figures 1 and 2 are reported the spectra for the LFP experiments with sulfoxides **1** and **6** (time-resolved spectra for the 3-CN-NMQ$^+$/toluene/**2**−**5**, **7** systems are reported in Figures S1−S5 in Supporting Information).

After the laser pulse, two main absorption bands were detected at 360−420 and 480−600 nm. The band centered at around 390 nm can be assigned to 3-CN-NMQ$^\bullet$, produced in the one-electron reduction of 3-CN-NMQ^{+*} by the aryl sulfoxide.[6] The band centered at ca. 520 nm is due to the sulfoxide radical cation on the basis of the spectral comparison with those of aryl sulfoxide radical cations reported in the literature.[3a,6,7] In the LFP experiments with sulfoxides **1**−**4** a weak absorption is also evident at 460 nm, that becomes slightly more pronounced for $\mathbf{1}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$. This band can be likely assigned to the phenylsulfinyl radical PhSO$^\bullet$.[15] In the photosensitized oxidation of **1**, kinetic analysis of the transient signal recorded at 510 nm within 15 μs after the laser pulse (Figure 1, inset b) showed an initial fast decay of the radical cation, followed by a slower decrease of absorbance which might be attributed to the decay of PhSO$^\bullet$. As observed in Figure 1, and in Figures S1−S3 in Supporting Information, the initial 390 nm absorption was replaced by a residual slower decaying absorption at ca. 370 nm (Figure 1, inset a), which can be assigned to the more stable phenyl sulfenate anion formed according to eq 2.

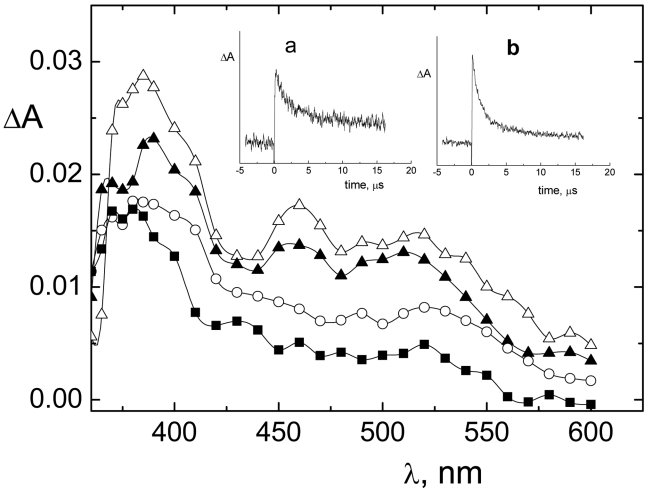


Figure 1. Time-resolved absorption spectra for the oxidation of **1** (1.0×10^{-2} M) photosensitized by 3-CN-NMQ$^+$ (7×10^{-4} M) in N$_2$-saturated CH$_3$CN in the presence of toluene (1 M), recorded 0.08 (△), 0.94 (▲), 2.6 (○), and 6.3 (■) μs after the laser pulse (λ_{ecc} = 355 nm). Inset: (a) decay kinetics recorded at 390 nm, (b) 510 nm.

In the LFP experiment with sulfoxides **5** and **6** no bands were observed that could be assigned to the arylsulfinyl radicals. The 4-methoxyphenyl sulfinyl radical absorbs at 515 nm,[15] and its band is probably superimposed with that of the radical cation $\mathbf{5}^{+\bullet}$, while 4-methylphenylsulfinyl radical absorbs out of the detectable wavelength region.[15] The absorption spectrum of the

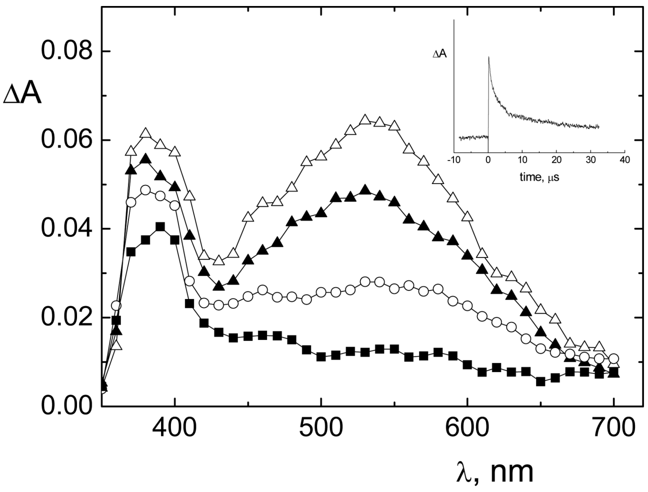


Figure 2. Time-resolved absorption spectra for the oxidation of **6** (1.0 × 10^{-2} M) photosensitized by 3-CN-NMQ$^+$ (7 × 10^{-4} M) in N_2-saturated CH_3CN in the presence of toluene (1 M), recorded 0.18 (△), 0.56 (▲), 1.71 (○), and 6.46 (■) μs after the laser pulse (λ_{ecc} = 355 nm). Inset: decay kinetics recorded at 510 nm.

radical 4-Br-$C_6H_4SO^\bullet$ is unknown, but it is likely similar to that of 4-Cl-$C_6H_4SO^\bullet$ (λ_{max} = 460 nm).[15] This would explain why also in the LFP experiment with **7** a residual absorption at 370 nm was observed at longer delay times, which could be confidently assigned to the 4-bromophenyl sulfenate.

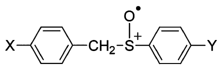
The rate constants for the decay of $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$ (k_d) were determined at a wavelength higher (550−620 nm) than that corresponding to the λ_{max} of the radical cations (see Figures S6−S12 in Supporting Information), to reduce the overlap of the absorption of the radical cation with that of $ArSO^\bullet$. In all cases, the decay kinetics followed first-order laws. The decay rate constants are collected in Table 2. The rate constants for the decay of the radical cation $\mathbf{2}^{+\bullet}$ were also determined in the presence of small amounts of H_2O as cosolvent (1−5%, v/v), and an increase of the k_d values was observed by increasing the amount of the cosolvent.

Theoretical Calculations. Neutral Sulfoxides. The C−S BDEs for the neutral aryl benzyl sulfoxides **1**, **3**−**7** were obtained by DFT calculations (the C−S BDE for **2** was previously reported[6]) at the B3P86/6-311+G(d,p)//B3P86/6-311+G(d,p) level of theory using the Gaussian 03 package.[17] The B3P86 functional was selected because it is known that it can be used with reasonable success for the BDE evaluation for a variety of C−X bonds[18,19] including C−S bonds.[19] The C−S BDEs are needed to estimate the C−S bond dissociation free energies (BDFEs) for the aryl benzyl sulfoxide radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$. The C−S BDEs of **1**−**7**, obtained from the calculations, are reported in Table 2 together with the BDFEs of the corresponding radical cations.

C−S BDEs for the neutral sulfoxides have been used to evaluate the C−S BDFEs in CH_3CN by the thermochemical cycle shown in Figure 3. Before starting the BDEs calculations, all the conformers of the sulfoxides and of the corresponding radicals formed in the C−S scission process have been identified by following a procedure reported in a previous study.[7]

The number of conformers found for sulfoxides were four for **1**, two for **3**, two for **4**, five for **5**, four for **6**, and two for **7**. Only one conformer was found for each benzyl radical 4-X-

Table 2. Decay Rate Constants (k_d) of Aryl Benzyl Sulfoxide Radical Cations ($\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$) Generated in the Oxidation of 1−7 Photosensitized by 3-CN-NMQ$^+$ (λ_{ecc}= 355 nm), Oxidation Potentials of Benzyl Radicals 4-$XC_6H_4CH_2^\bullet$ ($E_{1/2}^{ox}$), Oxidation Potentials (E_p), C−S Bond Dissociation Energies (BDEs) for the Aryl Benzyl Sulfoxides 1−7, and C−S Bond Dissociation Free Energies (BDFEs) for Radical Cations $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$

	k_d (10^5 s^1)[a]	$E_{1/2}^{ox}$ [b,c]	E_p [b,d]	C-S BDE (1-7)[e,f]	C-S BDFE ($1^{+\bullet}$-$7^{+\bullet}$)[f,g]
$\mathbf{1}^{+\bullet}$ X=Me, Y=H	12	0.51	1.77	29.8	-9.2
$\mathbf{2}^{+\bullet}$ X=H, Y=H	11 15[i] 18[j] 20.3[k] 22[l] 24[m]	0.73	1.90	29.9	-7.1[h]
$\mathbf{3}^{+\bullet}$ X=Cl, Y=H	9	0.80	1.99	29.7	-7.7
$\mathbf{4}^{+\bullet}$ X=CN, Y=H	5.8	1.08	2.10	28.9	-4.7
$\mathbf{5}^{+\bullet}$ X=H, Y=MeO	1.9	0.73	1.65	29.5	-1.7
$\mathbf{6}^{+\bullet}$ X=H, Y=Me	4.5	0.73	1.85	29.6	-6.2
$\mathbf{7}^{+\bullet}$ X=H, Y=Br	13	0.73	1.93	30.0	-7.7

[a] From LFP experiments in N_2-saturated CH_3CN; [sulfoxide] = 1.0 × 10^{-2} M, [3-CN-NMQ$^+$$ClO_4^-$] = 7 × 10^{-4} M, [toluene] = 1.0 M. [b] V vs SCE in CH_3CN. [c] Reduction potential of the 4-X-benzyl cations from ref 16. [d] Peak oxidation potential of aryl benzyl sulfoxides **1**−**7** measured by cyclic voltammetry (see Experimental Section). [e] From DFT calculations, see text. [f] kcal mol^{-1}. [g] At 298 K. [h] The value of −9.6 kcal mol^{-1}, calculated using the E_p value of methyl phenyl sulfoxide (2.0 V vs SCE) and reported in ref 6, has been recalculated using the E_p value measured for **2** (1.9 V vs SCE). [i] In the presence of 1% (v/v) H_2O. [j] In the presence of 2% (v/v) H_2O. [k] In the presence of 3% (v/v) H_2O. [l] In the presence of 4% (v/v) H_2O. [m] In the presence of 5% (v/v) H_2O.

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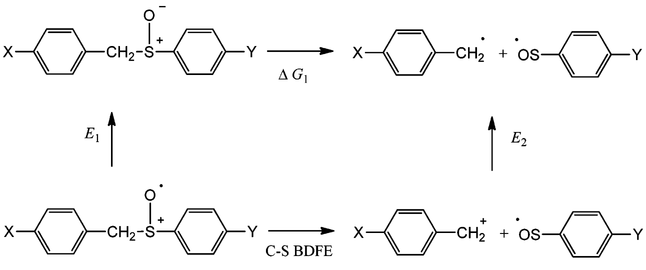


$$\text{C-S BDFE} = \Delta G_1 + F(E_2 - E_1) \qquad \Delta G_1 = \text{C-S BDE} - T\Delta S$$

Figure 3. Thermochemical cycle for the calculation of C−S BDFE values of aryl benzyl sulfoxide radical cations $1^{+\bullet}$−$7^{+\bullet}$.

$C_6H_4CH_2^\bullet$ (X = CH_3, Cl, CN). The structures and the energies for the arylsulfinyl radicals 4-Y-$C_6H_4SO^\bullet$ (Y = OCH_3, CH_3, H, Br) and the benzyl radical $PhCH_2^\bullet$ were reported in previous studies.[6,7]

Sulfoxide Radical Cations. With the aim to obtain energy and geometry of the minima, charges and spin distributions for sulfoxide radical cations $1^{+\bullet}$−$7^{+\bullet}$, DFT calculations, at the B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, were carried out. The level of theory was the same as that used in previous studies on aryl sulfide radical cations[9a,b] and aryl *tert*-butyl sulfoxide radical cations.[7]

The geometry optimization of each radical cation was carried out starting from the geometry of the corresponding neutral sulfoxide. The number of conformers found for sulfoxide radical cations $1^{+\bullet}$−$7^{+\bullet}$ were four for $1^{+\bullet}$, two for $2^{+\bullet}$, two for $3^{+\bullet}$, two for $4^{+\bullet}$, five for $5^{+\bullet}$, four for $6^{+\bullet}$, and two for $7^{+\bullet}$. The structures, dihedral angles, and bond lengths of the most stable conformers of $1^{+\bullet}$−$7^{+\bullet}$ are reported in Figures S13−S16 and Table S1 in Supporting Information. Following a procedure previously reported,[7] we were able to locate the transition state for the C−S bond cleavage in the radical cations $1^{+\bullet}$−$7^{+\bullet}$.

In Table 3 are displayed the C−S bond distances (d(C−S)), relative energies (E_{rel}) for the most stable conformers of radical cations $1^{+\bullet}$−$7^{+\bullet}$ and for the corresponding transitions states (TS) for the C−S bond fragmentation process.

Table 3. C−S Bond Distances (d(C−S)) and Relative Energies (E_{rel}) for the Most Stable Conformers of Radical Cations $1^{+\bullet}$−$7^{+\bullet}$ and for the Corresponding Transitions States (TS) for the C−S Bond Fragmentation Process

	d(C−S), Å	E_{rel},[a] kcal mol^{-1}
$1^{+\bullet}$	2.532	0
$1^{+\bullet}$ (TS)	3.259	0.77
$2^{+\bullet}$	2.217	0
$2^{+\bullet}$ (TS)	4.589	2.25
$3^{+\bullet}$	2.158	0
$3^{+\bullet}$ (TS)	4.118	1.37
$4^{+\bullet}$	2.086	0
$4^{+\bullet}$ (TS)	4.130	2.83
$5^{+\bullet}$	2.063	0
$5^{+\bullet}$ (TS)	5.131	4.65
$6^{+\bullet}$	2.150	0
$6^{+\bullet}$ (TS)	5.015	3.16
$7^{+\bullet}$	2.156	0
$7^{+\bullet}$ (TS)	4.398	2.05

[a] Corrected for the ZPVE.

In Table 4 are displayed the NPA charges (q_{NPA}) and spin densities for the most stable conformers of radical cations $1^{+\bullet}$−$7^{+\bullet}$ and for the corresponding transitions states (TS) for the C−S bond fragmentation process.

DISCUSSION

Formation of 4-X-benzyl alcohols and 4-X-benzyl acetamides as the main primary photoproducts in the steady-state photolysis experiments with all the sulfoxides investigated could be in accordance with a unimolecular C−S fragmentation process according to eq 1, as reported for the photosensitized oxidation of aryl *tert*-butyl sulfoxides and alkyl phenyl sulfoxides.[5−7] The precursor intermediate of both products is the 4-X-benzyl cation, formed by heterolytic C−S bond cleavage in the aryl benzyl sulfoxide radical cations, which reacts with CH_3CN or adventitious water (contained in the solvent) to produce benzyl acetamides and benzyl alcohols, respectively (Scheme 2, path a).[9] However, it should be considered that in fragmentation reactions of radical cations a mechanistic dichotomy is possible between a unimolecular and a bimolecular pathways.[20] Thus, in the presence of a primary benzyl group it cannot be excluded that the C−S fragmentation occurs by a solvent-assisted bimolecular process, a type of nucleophilic substitution where the leaving group is the sulfinyl radical (Scheme 2, path b). As shown in Table 1, the relative amounts of 4-X-benzyl alcohols and 4-X-benzylacetamides in the photochemical oxidation of **1**−**4** do not follow a regular trend. According to a unimolecular C−S bond cleavage, we should observe an increase of the relative amount of benzyl alcohol by increasing the stability of the 4-X-benzyl carbocation as expected for a less reactive and more selective species.[9b]

Formation of small amounts of 4-X-benzaldehydes with **1**−**7** was also detected in the reaction mixtures. These products might be formed by further oxidation of the primary benzylic photoproducts under the experimental condition. Another possible pathway leading to benzaldehydes involves a competitive β-C-H fragmentation in the radical cations $1^{+\bullet}$−$7^{+\bullet}$, leading to the α-arylsulfinyl benzyl radical.[21] This radical can be easily oxidized to the corresponding benzyl carbocation which might lead to the formation of an α-hydroxysulfoxide precursor of the final carbonyl derivative (Scheme 4). The first hypothesis is more likely, as supported by the previous observation that the benzaldehyde/benzyl alcohol molar ratio increases by increasing the irradiation time in the photosensitized oxidation of sulfoxide **2**.[6]

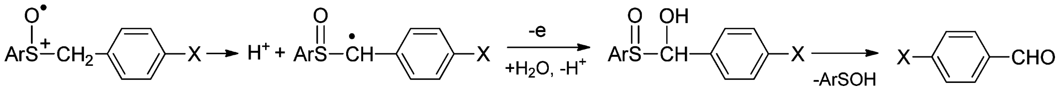
By considering first the series of 4-X-benzyl phenyl sulfoxide radical cations $1^{+\bullet}$−$4^{+\bullet}$, it can be observed, as expected, that both the reaction rates and the product yields increase by increasing the electron-releasing power of the substituent (see Tables 1 and 2). Moreover, the decay rate constants of radical cations $1^{+\bullet}$−$4^{+\bullet}$ are linearly correlated with the total benzylic product yields (see Figure S17 in Supporting Information). In the same order the BDFE values of the C−S bond in the sulfoxide radical cations become more negative on going from $4^{+\bullet}$ to $1^{+\bullet}$ (see Table 2). However, the substituent effects are not particularly high; in fact, the rate of C−S bond cleavage and the product yield increase only a factor of ca. 2 on going from $4^{+\bullet}$ to $1^{+\bullet}$. It is interesting to note that the small difference in $\Delta G^\ddagger$ between $4^{+\bullet}$ and $1^{+\bullet}$ (0.4 kcal mol^{-1}) is associated with a much higher difference in the C−S BDFE values (4.5 kcal mol^{-1}).

The analysis of the reaction rates and product yields for the series of benzyl 4-Y-phenyl sulfoxide radical cations $2^{+\bullet}$, $5^{+\bullet}$−

Table 4. NPA Charges (q_{NPA}) and Spin Densities for the Most Stable Conformers of Radical Cations $\mathbf{1}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ and for the Corresponding Transitions States (TS) for the C–S Bond Fragmentation Process

			q_{NPA}					spin				
	Y	Ar	S	O	benzyl	X	Y	Ar	S	O	benzyl	X
$\mathbf{1}^{+\bullet}$		0.018	1.110	−0.724	0.503	0.093		0.105	0.231	0.327	0.330	0.007
$\mathbf{1}^{+\bullet}$ (TS)		−0.023	0.950	−0.767	0.735	0.104		0.103	0.387	0.377	0.132	0.001
$\mathbf{2}^{+\bullet}$		0.057	1.212	−0.716	0.447			0.116	0.181	0.327	0.376	
$\mathbf{2}^{+\bullet}$ (TS)		−0.027	0.964	−0.776	0.839			0.108	0.411	0.326	0.155	
$\mathbf{3}^{+\bullet}$		0.054	1.226	−0.732	0.327	0.126		0.111	0.166	0.303	0.362	0.057
$\mathbf{3}^{+\bullet}$ (TS)		−0.025	0.955	−0.774	0.693	0.152		0.111	0.412	0.330	0.145	0.002
$\mathbf{4}^{+\bullet}$		0.086	1.259	−0.712	0.309	0.057		0.133	0.173	0.331	0.323	0.039
$\mathbf{4}^{+\bullet}$ (TS)		0.021	1.003	−0.758	0.668	0.066		0.094	0.361	0.285	0.250	0.009
$\mathbf{5}^{+\bullet}$	−0.086	0.295	1.251	−0.771	0.310		0.076	0.219	0.141	0.239	0.325	
$\mathbf{5}^{+\bullet}$ (TS)	−0.125	0.201	0.996	−0.782	0.710		0.019	0.087	0.347	0.261	0.286	
$\mathbf{6}^{+\bullet}$	0.084	0.017	1.234	−0.731	0.396		0.007	0.155	0.168	0.303	0.368	
$\mathbf{6}^{+\bullet}$ (TS)	0.068	−0.062	0.979	−0.780	0.795		0.002	0.108	0.389	0.300	0.201	
$\mathbf{7}^{+\bullet}$	0.191	−0.090	1.226	−0.736	0.409		0.048	0.131	0.161	0.292	0.369	
$\mathbf{7}^{+\bullet}$ (TS)	0.143	−0.157	0.963	−0.774	0.825		0.012	0.100	0.399	0.322	0.168	

Scheme 4



$\mathbf{7}^{+\bullet}$ clearly indicates that the effect of the para-substituent in the arylsulfinyl moiety is higher than that observed when the substituents are introduced in the benzyl ring of the sulfoxides. An increase of about 7 times in the C–S fragmentation rates (about 3 times in regard to the product yields) is noted on going from $\mathbf{5}^{+\bullet}$ to $\mathbf{7}^{+\bullet}$ (see Tables 1 and 2). Also in this series a linear correlation between the decay rate constants of radical cations $\mathbf{2}^{+\bullet}$, $\mathbf{5}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ and the total benzylic product yields can be drawn (see Figure S18 in Supporting Information). As expected, the decay rate constants decrease by increasing the electron-donating power of the substituents that is by increasing the stability of the radical cations. It has to be noted that a similar effect was observed in the C–S bond cleavage of aryl *tert*-butyl sulfoxide radical cations where the fragmentation occurs by a unimolecular process.[7] Also for this series of sulfoxides, a small difference in $\Delta G^{\ddagger}$ (ca. 1.1 kcal mol^{-1}) is associated with a substantial difference in BDFE (6 kcal mol^{-1} between $\mathbf{5}^{+\bullet}$ and $\mathbf{7}^{+\bullet}$).

Theoretical calculations of the same type performed for aryl *tert*-butyl sulfoxide radical cations (B3LYP/6-311G(d,p))[7] have been now extended to the series of aryl benzyl sulfoxide radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ to get information on the energetic of the C–S bond dissociation and to provide a possible explanation of the observed substituent effects on the C–S fragmentation rate constants. From a first look at the data of Table 4, it can be observed that NPA charges and spin populations are mainly localized on the sulfinyl group in both the series of radical cations with the exception of $\mathbf{1}^{+\bullet}$ where the charge and spin density on the benzyl moiety exceeds that on the sulfinyl group. However, a significant delocalization of the charge and spin also occurs in the benzyl group. As expected, the amount of charge and spin delocalized on the benzyl group increase by increasing the electron donating power of the X substituent in the series of radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{4}^{+\bullet}$ and decrease by increasing the electron donating power of the Y substituent in the series of radical cations $\mathbf{2}^{+\bullet}$, $\mathbf{5}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ (see Table 4).

By DFT calculations it was possible, following the unimolecular C–S fragmentation pathway, to locate the transition states for such fragmentation process in radical cations $\mathbf{1}^{+\bullet}$–$\mathbf{7}^{+\bullet}$. Thus, the energies, the charge and spin distributions for all the transition states were calculated. The data reported in Table 3 clearly shows that the E_{rel} for the TSs decrease as the BDFEs of the C–S bond cleavage process become more negative (earlier transition states along the reaction coordinate). If we compare, for example, the TS of the C–S bond cleavage for $\mathbf{1}^{+\bullet}$ (C–S BDFE = −9.2 kcal mol^{-1}) and $\mathbf{4}^{+\bullet}$ (C–S BDFE = −4.7 kcal mol^{-1}), the E_{rel} values and the degree of elongation of the C–S bond[23] are 0.77 kcal mol^{-1} and 28% for $\mathbf{1}^{+\bullet}$ and 2.83 kcal mol^{-1} and ca. 98% for $\mathbf{4}^{+\bullet}$. On the same line in the series of radical cations $\mathbf{2}^{+\bullet}$, $\mathbf{5}^{+\bullet}$–$\mathbf{7}^{+\bullet}$ the E_{rel} values and the degree of elongation of the C–S bond increase from 2.05 kcal mol^{-1} and 104% for $\mathbf{7}^{+\bullet}$ to 4.65 kcal mol^{-1} and ca. 150% for $\mathbf{5}^{+\bullet}$. A careful analysis of the data reported in Table 3 shows that even with relatively late TS, characterized by an higher degree of elongation of the C–S bond and by a more significant transfer of positive charge to the benzyl moiety in the TS, the kinetic effect of the substituent is relatively small.

The E_{rel} values calculated for the unimolecular C–S fragmentation process parallel the activation free energy values ($\Delta G^{\ddagger}$) calculated from the experimentally determined rate constants. However, if we compare the difference in E_{rel} values with those of the $\Delta G^{\ddagger}$ values, it can be easily noted that the former are significantly higher. For example, the difference in the E_{rel} for the two TS of $\mathbf{1}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ (ΔE_{rel} = 2.1 kcal mol^{-1}) corresponds to a difference of only 0.43 kcal mol^{-1} in the free energy of activation ($\Delta\Delta G^{\ddagger}$). In a similar way the ΔE_{rel} between $\mathbf{5}^{+\bullet}$ and $\mathbf{7}^{+\bullet}$ (2.6 kcal mol^{-1}) is much higher than that of $\Delta\Delta G^{\ddagger}$ (1.1 kcal mol^{-1}). All the discrepancies emerging from the comparison of theoretical calculations for the unimolecular C–S fragmentation process with the kinetic experimental results can be rationalized by considering the alternative, solvent-assisted bimolecular C–S bond cleavage

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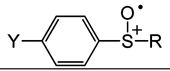
process with the solvent that might level off the decay rates of the radical cations **1**$^{+\bullet}$–**7**$^{+\bullet}$.

To obtain more insight about the involvement of a bimolecular process in the C–S fragmentation process of benzyl aryl sulfoxide radical cations, it is useful to compare the kinetic and thermodynamic data for C–S bond cleavage of aryl benzyl (**2**$^{+\bullet}$, **5**$^{+\bullet}$–**7**$^{+\bullet}$) and the corresponding aryl *tert*-butyl sulfoxide radical cations (4-Y-$C_6H_4SOC(CH_3)_3^{+\bullet}$, **8**$^{+\bullet}$–**11**$^{+\bullet}$)[7] (Table 5).

Table 5. Decay Rate Constants (k_d), C–S Bond Dissociation Free Energies (BDFEs), and Relative Energies (E_{rel}) of the Transition State (TS) for Aryl Benzyl Sulfoxide Radical Cations (2$^{+\bullet}$, 5$^{+\bullet}$–7$^{+\bullet}$)[a] and Aryl *tert*-Butyl Sulfoxide Radical Cations (8$^{+\bullet}$–11$^{+\bullet}$)[b] Generated by Oxidation of 2, 5–11 Photosensitized by 3-CN-NMQ$^+$ (λ_{ecc} = 355 nm)

	k_d (10^5 s^1)	C-S BDFE radical cations[c]	E_{rel}[c]
2$^{+\bullet}$ R=Bz, Y=H	11	-7.1	2.25
5$^{+\bullet}$ R=Bz, Y=MeO	1.9	-1.7	4.65
6$^{+\bullet}$ R=Bz, Y=Me	4.5	-6.2	3.16
7$^{+\bullet}$ R=Bz, Y=Br	13	-7.7	2.05
8$^{+\bullet}$ R=*t*Bu, Y=H	12	-18.1	0.83
9$^{+\bullet}$ R=*t*Bu, Y=MeO	1.9	-12.3	2.61
10$^{+\bullet}$ R=*t*Bu, Y=Me	4.1	-16.9	1.32
11$^{+\bullet}$ R=*t*Bu, Y=Br	18	-19.9	0.79

[a] This work. [b] From ref 7. [c] kcal mol^{-1}.

The decay rate constants of the aryl benzyl sulfoxide radical cations practically match that of the aryl *tert*-butyl sulfoxide radical cations with the same substituent on the arylsulfinyl ring. Indeed we should expect significantly smaller C–S fragmentation rates for **2**$^{+\bullet}$, **5**$^{+\bullet}$–**7**$^{+\bullet}$ with respect to those of **8**$^{+\bullet}$–**11**$^{+\bullet}$, on the basis of the large difference in driving force (ca. 11 kcal mol^{-1} more negative for aryl *tert*-butyl sulfoxides with respect to aryl benzyl sulfoxides) and of the relative E_{rel} values for the transition states (1.4–2.0 kcal mol^{-1} higher for aryl benzyl sulfoxides with respect to aryl *tert*-butyl sulfoxides). The most plausible hypothesis that might explain this behavior is that the C–S fragmentation in aryl benzyl sulfoxide radical cations **2**$^{+\bullet}$, **5**$^{+\bullet}$–**7**$^{+\bullet}$ involving a primary benzylic carbon may take advantage of nucleophilic assistance by the solvent. Solvent assistance is not possible with aryl *tert*-butyl sulfoxide radical cations where the C–S bond fragmentation involves a nucleophilically inaccessible tertiary carbon atom.

Finally, additional evidence in support of the occurrence of a solvent-assisted C–S fragmentation process in aryl benzyl sulfoxide radical cations is provided by the observation that the decay rate constant for the radical cation **2**$^{+\bullet}$ increases by addition of small amounts of water, going from 1.1×10^6 s^{-1} in CH_3CN to 2.4×10^6 s^{-1} in CH_3CN in the presence of 5% H_2O (v/v). From the decay rate constants k_d determined for **2**$^{+\bullet}$ as a function of water concentration (Figure S19 in the Supporting Information), a second-order dependence was found with k_2 = 4.0×10^6 M^{-1} s^{-1}. It has to be noted that the same addition of 5% H_2O in CH_3CN had no effect on the decay rate constant of *tert*-butyl phenyl sulfoxide radical cation, where the C–S bond cleavage occurs by a unimolecular process.

■ CONCLUSIONS

Solvent nucleophilic assistance to C–S bond cleavage in sulfoxide radical cations has been pointed out for the first time in the oxidation of aryl benzyl sulfoxides photosensitized by 3-cyano-*N*-methylquinolinium perchlorate on the basis of the results of steady-state and laser flash photolysis studies. The decrease of the decay rate constants (k_d) of aryl benzyl sulfoxide radical cations observed by increasing the electron-donating power of the arylsulfinyl substituent or by increasing the electron-withdrawing power of the benzylic substituent is too modest to be in line with a unimolecular fragmentation process. Accordingly, the ΔE_{rel} values for the TSs of the unimolecular C–S bond cleavage are significantly higher than the $\Delta\Delta G^‡$ values calculated from the experimentally determined rate constants. In addition the similar k_d values determined for aryl benzyl sulfoxide and aryl *tert*-butyl sulfoxide radical cations containing the same arylsulfinyl substituent are not in accordance with the significantly more negative C–S BDFE values calculated for aryl *tert*-butyl sulfoxide radical cations. The different decay process occurring in the two series of aryl sulfoxide radical cations is also demonstrated by the observation that the decay rate constant for benzyl phenyl sulfoxide radical cation increases by addition of small amounts of water, whereas the same addition had no effect on the decay rate constant of *tert*-butyl phenyl sulfoxide radical cation.

■ EXPERIMENTAL SECTION

Starting Materials. Aryl benzyl sulfides were prepared by reaction of benzyl chlorides with arylthiols in refluxing acetone in the presence of anhydrous K_2CO_3.[24] Oxidation of aryl benzyl sulfides with sodium periodate in aqueous ethanol afforded the corresponding aryl benzyl sulfoxides **1**–**7**.[25] Spectral data of substrates **1**–**7** are in accordance with literature data.[15,22h,26] Synthesis of 3-CN-NMQ$^+ClO_4^-$ was previously reported.[7,27] 4-X-Benzyl alcohols and 4-X-benzaldehydes are commercially available. 4-X-Benzylacetamides were prepared by reaction of 4-X-benzylamines with acetic anhydride[28] and characterized as reported in the literature.[28,29] Aryl arylthiosulfonates and aryl arylthiosulfinates were prepared as previously reported.[7] CH_3CN (spectrophotometric grade) was distilled over CaH_2.

Steady-State Photolysis. A Schlenk tube containing 1 mL of 3-CN-NMQ$^+ClO_4^-$ (1.0×10^{-3} M) and **1**–**7** (1.0×10^{-2} M) in N_2-saturated CD_3CN was irradiated in a photoreactor equipped with four phosphor-coated fluorescent lamps emitting at 355 ± 15 nm. Reaction mixtures were analyzed by ^1H NMR and HPLC after addition of an internal standard (bibenzyl). HPLC chromatography was performed with a HPLC system equipped with an UV–vis detector, and chromatograms were acquired at 230 nm wavelength. Compounds were eluted in a C18 column (5 μm, 4.6 × 250 mm), equilibrated with CH_3OH/H_2O (75/25), with an ascending gradient of CH_3OH (75–100%) at a flow rate of 0.7 mL/min. The following products were identified by comparison with authentic specimens: 4-X-benzyl alcohol, 4-X-benzylacetamide, 4-X-benzaldehydes, diaryl disulfides, aryl arylthiosulfonates, aryl arylthiosulfinates. The benzylic photoproducts were quantified by ^1H NMR. A satisfactory material balance (>90%) was observed in all the experiments. Solution irradiated in the absence of the photosensitizer did not show product formation in all cases.

Cyclic Voltammetry. E_p values were obtained by cyclic voltammetry experiments, conducted with a potentiostat controlled by a programmable function generator (cyclic voltammetry at 100 mV s^{-1}, 1 mm diameter platinum disc anode, and SCE as reference) in CH_3CN–$LiClO_4$ (0.1 M).

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Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were carried out with a laser kinetic spectrometer using the third harmonic (355 nm) of a Q-switched Nd:YAG laser delivering 7 ns pulses. The laser energy was <3 mJ per pulse. In all the experiments a 3 mL quartz cell containing a solution of **1**−**7** (1.0×10^{-2} M), 3-CN-NMQ$^+$ClO$_4^-$ (7×10^{-4} M), and the cosensitizer toluene (1 M) in N_2-saturated CH_3CN was flashed at 22 ± 2 °C. The transient spectra were obtained by a point-to-point technique, monitoring the ΔA values after the laser flash at 10 nm intervals, averaging at least 10 decays at each wavelength. The estimated error for the decay rate constants was ±10%.

Computational Details. Harmonic vibrational frequencies were calculated, at the B3P86/6-311+G(d,p) level of theory, to check that the stationary points found for neutral sulfoxides and radicals correspond to local minima and to evaluate the zero-point vibrational energy (ZPVE) corrections. The ZPV energies were scaled by a 0.9845 factor.[30] When, for a given compound, more than one minimum was found, its energy ($E_{el} + E_{ZPVE}$) was obtained by Boltzmann averaging the energy ($E_{el} + E_{ZPVE}$) of all the corresponding minima. It was verified that the stationary points found for sulfoxide radical cations correspond to local minima by calculating the harmonic vibrational frequencies at the B3LYP/6-311G(d,p) level of theory. The atomic charges were evaluated by natural population analysis (NPA).[31] Electron spin densities were evaluated using the Mulliken population analysis. In Supporting Information are reported the Cartesian coordinates, the electronic energy, and the zero-point vibrational energy of all the minima found.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Time-resolved absorption spectra after LFP of the 3-CN-NMQ$^+$/toluene/**2**−**7** systems in CH_3CN. Decay kinetics of $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$, LFP of the 3-CN-NMQ+/toluene/**1**−**7** systems, and structures, dihedral angles, and bond lengths of the most stable conformers of $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$. Cartesian Coordinates, energies, ZPVE from DFT calculations for neutral sulfoxides **1**, **3**−**7**, for arylsulfinyl and alkyl radicals, for sulfoxide radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$, and for the transition state of the C−S bond cleavage in the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{7}^{+\bullet}$. Linear correlation between the decay rate constants for the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, $\mathbf{5}^{+\bullet}$−$\mathbf{7}^{+\bullet}$ with the total benzylic product yields. Second-order plot for the decay of $\mathbf{2}^{+\bullet}$ as a function of water concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) The reduction potential of 3-CN-NMQ$^+$ (−0.60 V vs SCE in CH_3CN)[11] is much lower than that of PhSO$^\bullet$ (1.08 V vs SCE in CH_3CN, calculated at 25 °C on the basis of a thermochemical cycle).[6] Given the remarkable difference in the redox potential values for the two species, reaction 2 is expected to be very exergonic even in the presence of electron-donating substituents in the arylsulfinyl ring (4-MeO-$C_6H_4SO^\bullet$ and 4-Me-$C_6H_4SO^\bullet$).

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