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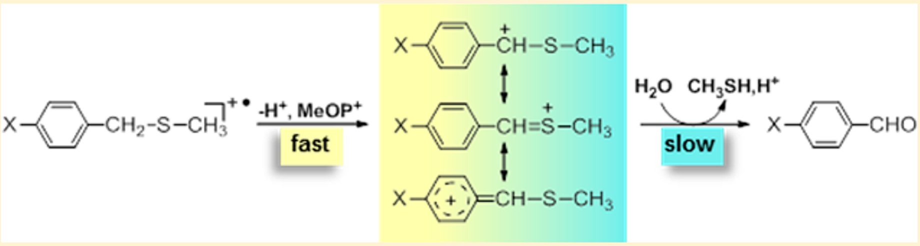
Photoinduced One-Electron Oxidation of Benzyl Methyl Sulfides in Acetonitrile: Time-Resolved Spectroscopic Evidence for a Thionium Ion Intermediate

Marta Bettoni,[†] Tiziana Del Giacco,*[,‡,§] Marina Stradiotto,[‡] and Fausto Elisei[‡,§]

[†]Dipartimento di Ingegneria Civile ed Ambientale, [‡]Dipartimento di Chimica, Biologia e Biotecnologie, and [§]Centro di Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, 06123 Perugia, Italy

S Supporting Information

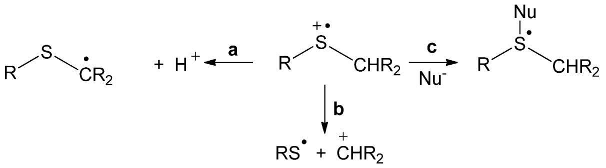


ABSTRACT: The photo-oxidation of 4-methoxybenzyl methyl sulfide (**1a**), benzyl methyl sulfide (**1b**), and 4-cyanobenzyl methyl sulfide (**1c**) has been investigated in the presence of *N*-methoxy phenanthridinium hexafluorophosphate ($MeOP^+PF_6^-$) under nitrogen in CH_3CN. The steady-state photolysis experiments showed for the investigated sulfides exclusively the formation of the corresponding benzaldehyde as the oxidation product, reasonably due to a deprotonation of the sulfide radical cations. Photo-oxidation of **1a**−**1c** occurs through an electron transfer process. Indeed, laser flash photolysis measurements showed an efficient formation of sulfide radical cations, detected in their dimeric form $[(4\text{-X-}C_6H_4CH_2SCH_3)_2^{+\bullet}]$ at ≈520 nm. At longer delay times, the absorption of the dimer radical cation was replaced by an absorption band assigned to the (α-thio)benzyl cation (thionium ion, λ_{max} = 420−400 nm), formed by oxidation of the benzyl radical and not by that of the (α-thiomethyl)benzyl radical, as expected if a C_α−H bond cleavage is operative. This finding highlights a particular stability of this kind of cation never reported before, even though its involvement in one-electron oxidation mechanisms of various sulfides has already been invoked. Density functional theory calculations allowed identification of a significant charge and spin delocalization involving both the phenyl ring and the sulfur atom of the radical cations.

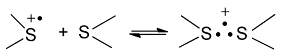
INTRODUCTION

Organic sulfur radical cations are important intermediates in a great variety of chemical processes, extending from those of industrial importance to the synthetic and biological ones.[1] Most studies have been carried out on the main reaction pathways of dialkyl sulfide radical cations; more recently, radical cations from aromatic sulfides (aryl sulfides having general formula ArSR) have attracted considerable attention.[2] These intermediates, investigated after generation by photoinduced electron transfer, radiolysis, or chemical and electrochemical oxidation of sulfides, can decay through competitive pathways whose relative rate constants depend strongly on the structure of the substrate and the experimental conditions (solvent polarity, additives, etc.). Generally, sulfide radical cations undergo the most common deprotonation reaction, which involves the cleavage of a C−H bond in the β position with respect to the sulfur atom (center of positive charge), together with the breaking of the C−S bond (α cleavage), which leads to the formation of a sulfenyl radical and a carbocation (Scheme 1, paths a and b, respectively). Moreover, these intermediates can be attached at the sulfur by nucleophilic species (Scheme 1, path c), as oxygen and superoxide anion to form sulfoxides.[3]

Scheme 1



In particular, nucleophiles such as sulfides can quickly attack the sulfur radical cations, forming dimeric three-electron-bonded complexes (two bonding σ and one antibonding σ^* electrons), which are known to establish an equilibrium with the molecular radical cation as formulated in eq 1. Asmus et al.



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have reported numerous examples which substantiated, by experimental data and theoretical considerations, that the

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radical cations of aliphatic sulfides are stabilized by the formation of a sulfur−sulfur three-electron bond.[4] Sawaki et al. have argued the formation of dimers also from aromatic sulfides (with a sulfur atom bound to an aromatic ring).[5] They have investigated radical cations of thioanisoles by laser flash photolysis and reported that both the σ- and π-type dimers are formed depending on the structure and concentration. More recent studies have further confirmed these results.[2h,3d,6]

Along this line, we have considered it worthwhile to extend these investigations to the one-electron photo-oxidation of benzyl methyl sulfides **1a−1c**, with different substituents in *para* position on the ring, by $MeOP^+PF_6^-$ in CH_3CN under nitrogen. These reactions have been studied by nanosecond laser flash photolysis (LFP) and steady-state photolysis. The transient species produced, their decay pathways, and the final photoproducts have been identified. The results of this study, reported herein, have been integrated by DFT calculations in order to obtain information on the geometry of the radical cations and, more importantly, the charge and spin distribution. This information was considered to be of great utility to better understand the dynamics of the radical cation fragmentation process and, in particular, the SOMO position.

■ RESULTS

Steady-State Photolysis. Steady-state photolysis experiments were carried out at 355 nm by irradiating a N_2-saturated CH_3CN solution of sulfides **1a−1c** in the presence of $MeOP^+PF_6^-$. As already reported,[7] in these experimental conditions, the singlet excited state of *N*-methoxyphenanthridinium was produced, which undergoes breaking of the N−O bond, forming the phenanthridinium radical cation ($P^{+\bullet}$). This species is a quite powerful oxidant (the estimated reduction potential is 2.0 V vs SCE in CH_3CN)[7a] that is able to accept one electron from the investigated sulfides because they have lower oxidation potentials (Table 1), thus forming the corresponding sulfide radical cations (Scheme 2), highlighted by LFP studies.

Table 1. Chemical Yields (%) of the Photoproducts, Relative Rate (k_X/k_H), and Oxidation Potentials (E_p) for the $MeOP^+$-Sensitized Photo-oxidation Reaction of Benzyl Methyl Sulfides 1a−1c in N_2-Saturated CH_3CN

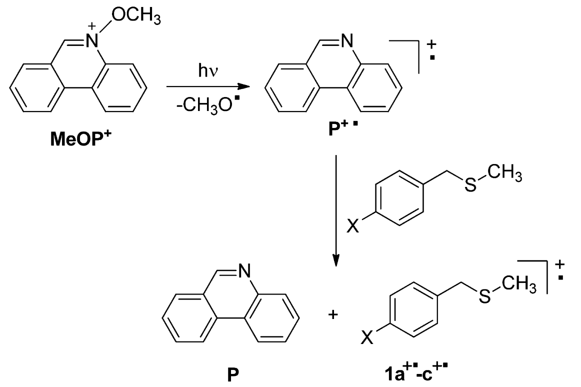
sulfide	unreacted sulfide[a] (%)	$X\text{-}C_6H_4CHO$[a] (%)	k_X/k_H[b]	E_p[c] (V)
1a (X = OCH_3)	77	17	2.25	1.55
1b (X = H)	83	16	1	1.63
1c (X = CF_3)	88	12	0.47	1.73

[a] [Sulfide] = 1.0×10^{-2} M, [$MeOP^+PF_6^-$] = 5.0×10^{-3} M. Yields refer to the initial amount of substrate. [b] Determined by kinetic competitive experiments (GC analysis of unreacted substrates). [Sulfide] = 5.0×10^{-3} M, [$MeOP^+PF_6^-$] = 5.0×10^{-3} M. [c] Oxidation peak potential vs SCE measured by cyclic voltammetry in air-equilibrated CH_3CN; sweep rate = 100 mV s^{-1}.

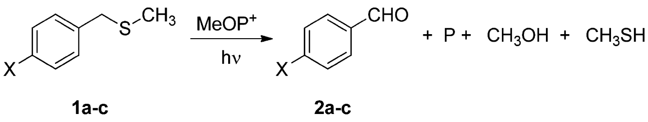
The photolysis of sulfides **1a−1c** produced benzaldehydes **2a−2c** as the only products (Scheme 3).[8] The products were identified with ^1H NMR and GC-MS techniques by comparison with authentic specimens.

Quantitative analysis, performed by GC using the internal standard method, showed a similar amount of benzaldehyde for each sulfide (17, 16, and 12% for **1a**, **1b**, and **1c**, respectively) after 15 min of irradiation (Table 1). The material balance was satisfactory (>94%) in all experiments.

Scheme 2

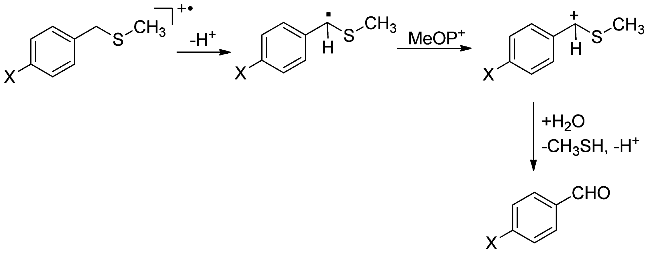


Scheme 3



The structure of photoproducts formed can reasonably be rationalized on the basis of the formation of the radical cation followed by benzylic deprotonation (Scheme 4), as already suggested by Albini et al.[9] for the oxidation of analogous ethyl sulfides ($PhCH_2SCH_2CH_3$) photosensitized by 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$).

Scheme 4



The resulting (α-thiomethyl)benzyl radical (4-X-C_6H_4-$CH^\bullet SCH_3$) is then oxidized, likely by the ground-state *N*-methoxyphenanthridinium (vide infra), to the corresponding cation, which forms the final product (benzaldehyde) by reaction with adventitious water. The disappearance of *N*-methoxyphenanthridinium was checked by recording the UV−visible absorption spectra before and after irradiation; this analysis endorsed the consumption of two $MeOP^+PF_6^-$ molecules for each molecule of sulfide. The sulfur-containing product CH_3SH was not identified experimentally because of its high volatility. Other detected products were those derived from the N−O fragmentation of $MeOP^+$ (phenanthridine, P, and methanol).

The relative reaction rates, expressed as ratio of the photo-oxidation rate constant of 4-X-$C_6H_4CH_2SCH_3$ (k_X) and that of the unsubstituted sulfide (k_H), were determined by the kinetic competitive method (Table 1). As shown in Figure S1 (see Supporting Information), log(k_X/k_H) values decrease linearly as the sulfide oxidation potential (E_p, Table 1) increases; this result is in line with a rate-determining electron transfer step from the benzyl methyl sulfide to the phenanthridinium radical cation (Scheme 2). The slope of −0.16 mol/kcal is characteristic of a substrate-like transition state in a slightly exergonic electron transfer.[10]

Laser Flash Photolysis Studies. Upon laser excitation (λ_{exc} = 355 nm) of N_2-saturated CH_3CN solutions of sulfides **1a**−**1c** (1.0×10^{-2} M) and $MeOP^+$ (1.4×10^{-4} M), a broad and intense absorption with a maximum around 520 nm was detected just after the laser pulse. As an example, the time-resolved spectra of the **1b**/$MeOP^+$ system are reported in Figure 1, while those of **1a** and **1c** are shown in Figures S2 and S3 (Supporting Information). It seems to be reasonable to attribute this absorption to the three-electron-bonded dimer radical cations, $[(ArCH_2,CH_3)S\therefore S(ArCH_2,CH_3)]^+$, formed according to eq 1. Indeed, the corresponding $[(CH_3)_2S\therefore S(CH_3)_2]^+$ structure, having a hydrogen atom in place of the aryl group, is reported to absorb at shorter wavelength (465 nm in aqueous solution),[11] but it is known that the electron induction, as could be exerted by the aryl group, into the three-electron (2σ, σ^*) bond can affect the energy of the $\sigma \rightarrow \sigma^*$ transition, which will result in a decrease in bond strength and then to a red shift in the absorption spectrum.[4b] The absorption bands of the molecular radical cations $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$, produced by fast oxidation of sulfides **1a**−**1c** due to the phenanthridine radical cation, which should be in rapid equilibrium with the dimer radical cations, should be around 300 nm,[12] an undetectable spectral position with our experimental setup. The decay rates of the dimer radical cations, thus corresponding to those of monomer radical cation $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$,[5,6a] were determined in the presence of nitrogen by following the kinetics at 600 nm. This wavelength, higher than that corresponding to the λ_{max}, was chosen in order to reduce the overlap of the dimer absorption with that of other transients (vide infra). In all cases, the decay kinetics followed clean first-order laws, in accordance with a unimolecular fragmentation process. The lifetimes (τ) measured at 25 °C are reported in Table 2.

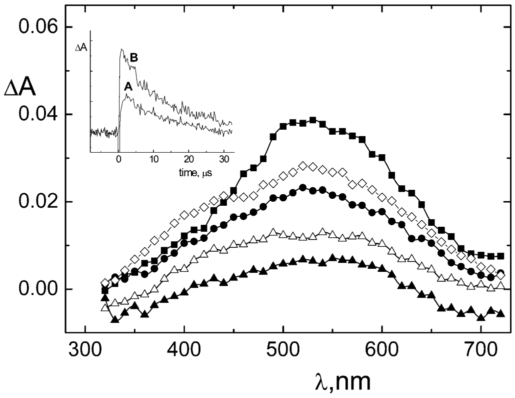


Figure 1. Time-resolved absorption spectra of the $MeOP^+$ (1.4×10^{-4} M)/**1b** (1.0×10^{-2} M) system in N_2-saturated CH_3CN recorded (■) 0.88, (◊) 2.5, (●) 7.4, (△) 18, and (▲) 32 μs after the laser pulse; λ_{exc} = 355 nm. Inset: decay kinetics recorded at (A) 400 and (B) 530 nm.

Table 2. Lifetimes of the Dimer Radical Cations Determined without (τ) and with the Presence of NO_3^- Base (τ_{base}) and of the Cations (τ_C) Formed in the $MeOP^+$-Sensitized Photooxidation Reaction of Benzyl Methyl Sulfides 1a−1c in N_2-Saturated CH_3CN[a]

	$[(ArCH_2,CH_3)S\therefore S(ArCH_2,CH_3)]^+$		$4\text{-X-}C_6H_4CH^+SCH_3$
sulfide	τ	τ_{base}[b]	τ_C
1a (X = OCH_3)	7.8	0.84	9.8
1b (X = H)	7.7	0.92	16
1c (X = CF_3)	7.3	0.91	12

[a] Values in μs. Experimental error of 10%. [b] $[Bu_4N^+NO_3^-] = 2.0 \times 10^{-2}$ M.

The time evolution of the absorption spectra showed a slow decay of the ΔA signal at 520−550 nm (see insets of Figure 1 and Figures S2 and S3) followed by the growth of the absorption in the 400−450 nm region. The assignment of the absorbance at 400−450 nm to the (α-thiomethyl)benzyl radical formed by deprotonation of the radical cations (Scheme 4) can be excluded on the basis of the following considerations. First, the time-resolved spectra in the 400−450 nm region (see Figure S4) were not influenced by oxygen, so that rules out the uncharged nature of the transients. In addition, the absorption maximum for this kind of radicals is expected at shorter wavelengths.[12] Actually, the experimental absorption spectra of $C_6H_5CH^\bullet SCH_3$ radical were obtained by photolysis of the dicumyl peroxide/**1b** system in CH_3CN, which produced the absorption spectra shown in Figure S5. As already reported,[13] irradiation of dicumyl peroxide with UV light promotes the formation of cumyloxyl radical $[C_6H_5C(CH_3)_2O^\bullet]$ within the laser pulse (eq 2), which displays a broad band at 490 nm. The time evolution of the absorption spectra shows that this signal decay ($t_{1/2}$ = 0.6 μs) is coupled with the growth of the absorption at 340 nm ($t_{1/2}$ = 0.4 μs) that can be reasonably attributed to the formation of $C_6H_5CH^\bullet SCH_3$ (eq 3).[14]

$$C_6H_5C(CH_3)_2O\text{-}OC(CH_3)_2C_6H_5 \xrightarrow{h\nu} 2C_6H_5C(CH_3)_2O^\bullet \quad (2)$$

$$C_6H_5C(CH_3)_2O^\bullet + C_6H_5CH_2SCH_3 \rightarrow C_6H_5C(CH_3)_2OH + C_6H_5C^\bullet HSCH_3 \quad (3)$$

On the other hand, with the addition of NO_3^- base (as tetra-n-butylammonium salt, TBAN, 2.0×10^{-2} M), the lifetimes of the cation radicals $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$ were significantly shortened, as expected. In fact, the decay rates of the radical cation dimers, recorded in the presence of TBAN at higher wavelengths (580−600 nm) than λ_{max} (in order to reduce the overlap of these transients with that absorbing at 400 nm), followed clean first-order kinetics (see insets C of Figure 2 and Figures S6 and S7) with lifetime values (see Table 2) about an order of magnitude lower than those obtained in the absence of NO_3^-. According to these results, there is a poor effect of the sulfide structure on the deprotonation rate of the radical cation dimers.

As observed, in the presence of NO_3^-, the radical cations generated a transient fully developed at about 0.7, 1.8, and 2.7 μs after the flash with λ_{max} at 420, 410, and 400 nm for **1a**, **1b**, and **1c**, respectively. The absorption spectra recorded just after the laser pulse appear as negative signals until ≈450 nm due to the bleaching of the $MeOP^+PF_6^-$ ground state. From the insets, it can be observed that the decay of the radical cations at λ = 580 nm for $\mathbf{1b}^{+\bullet}$ (inset C of Figure 2) and at 600 nm for $\mathbf{1a}^{+\bullet}$ and $\mathbf{1c}^{+\bullet}$ (insets C of Figures S6 and S7, respectively) is practically synchronous with the buildup of the transient at 400−420 nm (insets A of the corresponding figures). The effect of NO_3^- can be understood in terms of this anion acting as a Brönsted base with respect to the radical cation, endorsing the

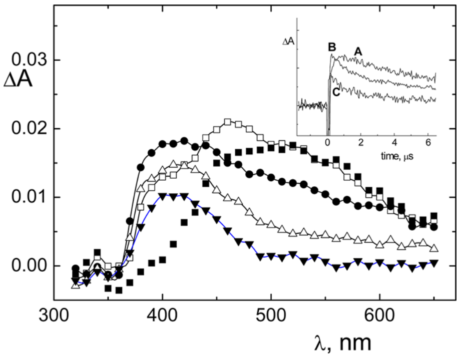


Figure 2. Time-resolved absorption spectra of the $MeOP^+$ (2.4×10^{-4} M)/**1b** (1.0×10^{-2} M) system in the presence of 2.0×10^{-2} M TBAN recorded (■) 0.18, (□) 0.22, (●) 1.8, (△) 3.0, and (▼) 6.4 μs after the laser pulse in N_2-saturated CH_3CN; λ_{exc} = 355 nm. Inset: decay kinetics recorded at (A) 400, (B) 450, and (C) 580 nm.

hypothesis of the deprotonation as the main reaction of the radical cation, responsible for the aldehyde formation (Scheme 4). These results lead us to attribute the bands centered around 400−420 nm to the (α-thio)benzyl cations, 4-X-$C_6H_4CH^+SCH_3$, obtained by oxidation of the corresponding (α-thio)benzyl radicals, formed by C_α−H cleavage of the radical cations. On the other hand, the bathochromic shift of the cation absorption bands of about 80 nm compared to that of the corresponding radicals is in line with what has already been observed with similar species.[16]

The kinetic decay recorded at 420 nm is not modified by the presence of oxygen, thus confirming the cationic nature of the transients (Figure S8 shows the oxygen effect on the decay rate recorded at 420 nm for **1a**). The missing evidence of 4-X-$C_6H_4CH^\bullet SCH_3$ in the time-resolved spectra suggests that the rate of its formation is slower than that of its disappearance. This aspect will be discussed in the Discussion section. The decay kinetics recorded at 400−410 nm were well fitted by first-order laws (lifetime values are collected in Table 2). The decay rate should be due to the reaction of the cation with the residual water present in CH_3CN to produce the only product observed by us in steady-state photolysis, 4-X-C_6H_4CHO (Scheme 4). Indeed, the lifetimes did not increase by addition of water, probably because the amount of water in our medium (≈2 × 10^{-2} M) is sufficiently high to completely trap the cation.[17]

Quantum Mechanical Calculations: Sulfide Radical Cations. The most significant geometrical features (dihedral angles and bond lengths, as defined in Figure 3) of radical cations $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$ are reported in Table 3. From these data, it can be observed that the conformations for the radical cations have very similar geometries. In all of the energy minimum conformations, the CH_2−S bond is almost perpendicular to the phenyl ring (the dihedral angle Φ is approximately 80°). The conformer at the minimum energy of $\mathbf{1b}^{+\bullet}$ is shown in Figure 4 ($\mathbf{1a}^{+\bullet}$ and $\mathbf{1c}^{+\bullet}$ conformers are reported in Figure S9 in Supporting Information).

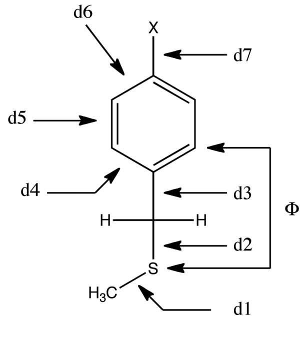


Figure 3. Definition of geometrical features of radical cations $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$ reported in Table 3.

The atomic charges were obtained by natural population analysis (NPA).[18] Unpaired electron spin densities were calculated using the Mulliken population analysis. From the NPA charges and spin density data obtained for radical cations $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$ and reported in Table 4, it can be noted that the charge and spin density of the radical cations are mainly localized on the Ar ring and sulfur. In particular, charge and spin density increase significantly on the sulfur atom (from 0.265 to 0.524 and from 0.361 to 0.749, respectively) at the expense of that on the Ar ring (from 0.538 to 0.103 and from 0.511 to 0.243, respectively) on going from the radical cation $\mathbf{1a}^{+\bullet}$ to $\mathbf{1c}^{+\bullet}$. A reasonable explanation of this distribution is that in the radical cation a through-space interaction between the aromatic ring and the sulfur p orbital takes place, favored from the conformational geometry. This specific interaction is well visualized in the SOMO-2 representation for $\mathbf{1b}^{+\bullet}$ shown in Figure 5 ($\mathbf{1a}^{+\bullet}$ and $\mathbf{1c}^{+\bullet}$ conformers are reported in Figure S10 in Supporting Information). The distribution of charge and spin between the ring and sulfur can also be represented as a contribution of the resonance structures I and II to the conformation of the radical cation (Scheme 5). Obviously, the higher the electron-donating power of the X substituent, the more the resonance structure II contributes to the resonance, as evidenced from the data of Table 4.[19]

Some hyperconjugative interaction could be assumed between the C_α−S bond and the π system of the aromatic ring, which can be represented by a contribution of structure III (Scheme 5). The very low charge on the CH_2 group (Table 4) suggests, however, that structure III should be a much less important contributor to the resonance hybrid of the radical cation conformations.

■ DISCUSSION

The results of the steady-state photolysis experiments have clearly indicated that in all cases benzaldehydes are formed as the major primary reaction products. The carbonyl compounds are supposed to come from oxidation followed by reaction with adventitious water of the (α-thiomethyl)benzyl carbon radical, which is formed by C_α−H bond cleavage in the radical cation (Scheme 4), the intermediate detected by laser flash photolysis experiments within the laser pulse. The possibility of cleavage of the C_α−S bond (to give a benzyl cation and a methylthiyl radical) of $\mathbf{1a}^{+\bullet}$−$\mathbf{1c}^{+\bullet}$, together with the deprotonation from the benzylic position, as observed with benzyl phenyl sulfide radical cations,[3d,e,22] can be experimentally excluded. This is in line with a deprotonation reaction that is much more exergonic than the C_α−S bond cleavage.[23]

The focus of this study has been to point out, by flash photolysis experiments, that the intermediate cation (4-X-$C_6H_4CH^+SCH_3$), and not its precursor (4-X-$C_6H_4CH^\bullet SCH_3$), is accumulated in the **1a**−**1c** photo-oxidation. In fact, Asmus et al. observed, by pulse radiolysis investigation, the $RSR(-H)^\bullet$ radical as an intermediate in the oxidation of dimethylsulfide and its derivatives by a hydroxyl radical, formed by deprotonation of the monomer radical cation or the dimer in

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Table 3. Most Significant Dihedral Angle (deg) and Bond Lengths (Å) of Radical Cations $1a^{+•}$−$1c^{+•}$ in AcN (CPCM Model) Optimized by B3LYP/6-311G(d,p)

	Φ	d_1	d_2	d_3	d_4	d_5	d_6	d_7
$1a^{+•}$	81	1.820	1.849	1.489	1.416	1.370	1.425	1.321
$1b^{+•}$	82	1.811	1.839	1.500	1.411	1.383	1.405	1.083
$1c^{+•}$	78	1.804	1.836	1.505	1.406	1.383	1.404	1.508

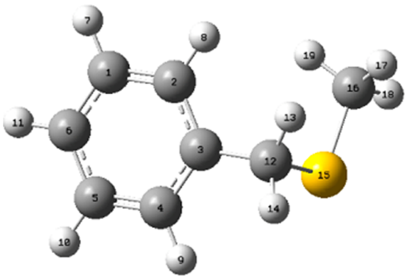


Figure 4. Conformer at the minimum of energy of $C_6H_5CH_2SCH_3^{+•}$ ($1b^{+•}$).

Table 4. NPA Charges (q_{NPA}) and Mulliken Spin Densities for the Most Stable Conformers of Radical Cations $1a^{+•}$−$1c^{+•}$

		X	C_6H_4	CH_2	S	CH_3
$1a^{+•}$ (X = OCH_3)	q_{NPA}	0.042	0.538	0.064	0.265	0.089
	spin	0.140	0.511	−0.019	0.361	0.007
$1b^{+•}$ (X = H)	q_{NPA}		0.311	0.097	0.450	0.141
	spin		0.369	0.017	0.640	−0.025
$1c^{+•}$ (X = CF_3)	q_{NPA}	0.110	0.103	0.098	0.524	0.165
	spin	0.002	0.243	−0.019	0.749	0.025

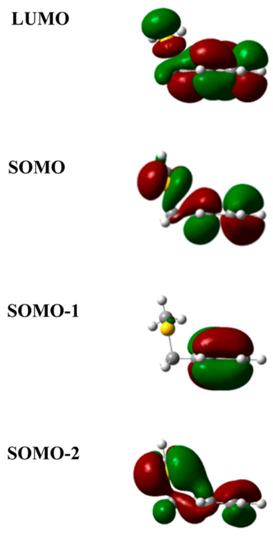
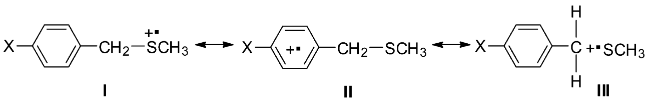


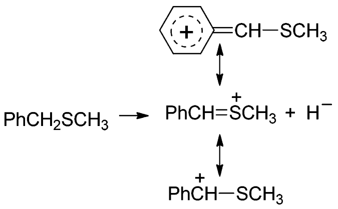
Figure 5. Molecular orbitals of the energy minimum conformer of $C_6H_5CH_2SCH_3^{+•}$ ($1b^{+•}$).

Scheme 5

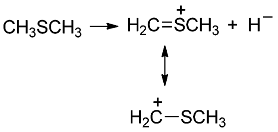


equilibrium with it (eq 1).[4a,f] This radical, probably present as a hybrid of mesomeric forms (−CH•−S− ↔ −CH=S•−), absorbed at 280 nm in aqueous solution. The formation of the corresponding cation $RSR(-H)^+$, as product of disproportionation of the radical $RSR(-H)^•$, was detected not with absorption measurements (no distinct band was identified on the spectrum) but by conductivity recording.[4f] The exclusive observation of the cation in our case may be traced back to a different stability of the thionium ions, as supported by a MNDO study performed on this kind of cation.[25] In particular, this theoretical treatment has shown that (α-thio)benzyl cation ($PhCH^+SCH_3$) is significantly more stable than the corresponding ion with hydrogen in place of phenyl ($CH_3SCH_2^+$). The effect of the phenyl substituent on the energetics of thionium ion formation was estimated by the ΔΔ*H* value, namely, the difference between the enthalpy change for the reactions shown in Schemes 6 and 7, quantified as −28 kcal/mol. The greater stability of $PhCH^+SCH_3$ is due to the fact that its structure can be described in terms of various mesomeric forms (Scheme 6), more numerous than those of $CH_3SCH_2^+$ (Scheme 7), as indicated by the values obtained by calculation of the π-bond orders for the two cation structures, equal to 0.60 for CH−S and 0.61 for C−Ph bonds in the benzyl cation and 0.86 for C−S and 0 for C−H bonds in the methylthiomethyl cation.[25]

Scheme 6



Scheme 7



Another interesting comparison is with the behavior of the corresponding aromatic thioether cations, $PhCH^+SPh$, an intermediate species whose formation has been invoked in the oxidation of aryl benzyl sulfides studied by pulse radiolysis and laser flash photolysis but has never been experimentally observed.[3d,e,h] This different behavior could be explained on the basis of the lower stability of $PhCH^+SPh$ with respect to $PhCH^+SCH_3$, as the feasible conjugation between the sulfur atom and the near aromatic π system could prevent an efficient intervention of the sulfur to the delocalization of the positive charge.

Another interesting observation is that the (α-thiomethyl)-benzyl radical, to be oxidized by the ground-state sensitizer (see Scheme 4), should have an oxidation potential more negative than that of $MeOP^+$ (−0.81 V vs SCE in MeCN, obtained from the corresponding *N*-ethyl structure),[7b] and this is in agreement with a very stable (α-thiomethyl)benzyl cation.[26] The oxidation potentials of similar radicals, such as $C_6H_5CH^{\bullet}OCH_3$ and $C_6H_5CH^{\bullet}OH$ (−0.33 and −0.30 V vs SCE in CH_3CN, respectively),[28,29] point out a significantly lower stability of the corresponding cations and would not make oxidation practicable.

From the decay kinetic data of radical cations **1a**$^{+\bullet}$−**1c**$^{+\bullet}$ reported in Table 2, it can be noted that the deprotonation rates are practically not affected by the substituent type, both in the absence and in the presence of the base (τ = 7/8 and 0.9 μs, respectively).[30] On the contrary, the deprotonation rate constant of the toluene radical cation ($PhCH_3^{+\bullet}$, $k = 1 \times 10^7$ s^{-1})[31] in water is nearly 5 orders of magnitude higher than that of 4-methoxytoluene ($4\text{-}CH_3O\text{-}C_6H_4CH_3^{+\bullet}$, $k = 4 \times 10^2$ s^{-1}),[32] taken as a reference. This remarkable dependence on the substituent is explainable considering that $4\text{-}CH_3O\text{-}C_6H_4CH_3^{+\bullet}$ becomes a weaker acid with respect to $PhCH_3^{+\bullet}$ because the methoxy group (an electron-donating substituent) decreases its reduction potential (1.71 compared to 2.35 V of toluene, both vs SCE in CH_3CN).[33] In other words, on the basis of these data, it can be stated that for radical cations of such structures the kinetic acidity parallels thermodynamic acidity. In the case of benzyl methyl and 4-methoxybenzyl methyl sulfide radical cations, the significant amount of spin and positive charge delocalized not only on the ring but also on the sulfur atom (as indicated by DFT calculations) makes the substituent effect weaker. This is reflected by the difference in oxidation potential between **1a** and **1b** (0.08 vs 0.64 V of the corresponding benzyl derivatives) and then on the kinetic acidity.

■ CONCLUSIONS

Radical cations **1a**$^{+\bullet}$−**1c**$^{+\bullet}$, photochemically generated by $MeOP^+$, were able to deprotonate and then to form the corresponding aldehyde compounds. Benzyl radicals, namely, the intermediates generally observed after the C_α−H bond cleavage, were not sufficiently accumulated to be detected by LFP experiments, but the corresponding (α-thio)benzyl cations (thionium ions) were highlighted, coming from their oxidation. In line with this assignment, the decay rate of these transients (a first-order process) was unaffected by oxygen, while their formation reactions were considerably accelerated by the intervention of a base (TBAN). This result has been explained by invoking the stability of the thionium ions, due to a delocalization of the positive charge extended to the whole structure. Until now, thionium ions had been pointed out by pulse radiolysis conductivity experiments to be intermediates in the oxidation of dialkyl sulfides, but their absorption spectra were never identified.

The lifetimes of the radical cations were very slightly sensitive to the nature of the substituent, both with and without base. These results have been rationalized by considering (DFT calculations) that charge and spin are delocalized among the ring and the sulfur atom, which leads to a resulting leveling of the acid strength of the benzylic position.

■ EXPERIMENTAL SECTION

Starting Materials. 4-Methoxybenzyl methyl sulfide (**1a**), benzyl methyl sulfide (**1b**), and 4-trifluoromethylbenzyl methyl sulfide (**1c**) were prepared by reaction of the corresponding benzyl mercaptans with CH_3I in ethyl alcohol according to the procedure described in the literature.[34] Substrates **1a** and **1b** were characterized as already described.[35] The purity of **1c** was checked by NMR and GC-MS analysis. **1c**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, 2H), 7.53 (d, 2H), 3.81 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 129.2, 128.8, 125.5, 124.2, 37.9; 14.9; GC-MS (70 eV, EI) *m/z* 206 (M^+, 46), 187 (5), 159 (100), 139 (4), 109 (21), 89 (5), 63 (5). Benzaldehydes **2a**−**c** and TBAN were commercially available. *N*-Methoxyphenanthridinium hexafluorophosphate was prepared according to a literature procedure.[7a,36] Acetonitrile of HPLC grade for product analysis and acetonitrile of spectrophotometric grade for spectroscopic measurements were used as received.

Steady-State Oxidation. A solution prepared by dissolving $MeOP^+PF_6^-$ (5.0×10^{-3} M) and benzylic sulfide (1.0×10^{-2} M) in 10 mL of MeCN was irradiated in an Applied Photophysics multilamp apparatus with six phosphor-coated fluorescent lamps (15 W each) emitting at 355 nm ($\Delta\lambda_{1/2}$ = 20 nm), at running water temperature (15 °C), with argon bubbling through the solution. After irradiation, the reaction mixture was analyzed after adding an internal standard (bibenzyl) by GC, GC-MS, and ^1H NMR, and all products formed were identified by comparison with authentic specimens. The sensitizer analysis was performed by optical density measurements on a HP-8451 diode array spectrophotometer. The material balance was always satisfactory (>94%).

Blank experiments, performed by keeping a solution of $MeOP^+PF_6^-$ and sulfide in the dark or by irradiation of solutions in the absence of the sensitizer, showed no formation of products.

Competitive Experiments. The kinetic experiments were performed at 20 °C by irradiating (as above) 10 mL of N_2-saturated CH_3CN solutions containing $MeOP^+PF_6^-$ (5.0×10^{-3} M) and the two substrates (both 5.0×10^{-3} M). The amounts of the products (benzaldehydes) were determined by GC with respect to an internal standard at different times, and the values were inserted into a suitable kinetic equation.[37] The reported k_{rel} values are the average of at least three determinations.

Laser Flash Photolysis. Excitation wavelength of 355 nm (from a Nd:YAG laser, Continuum, third harmonic, pulse width ≈7 ns and energy <3 mJ per pulse) was used in nanosecond flash photolysis experiments.[38] The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (ΔA) after the laser flash at intervals of 5−10 nm over the spectral range of 300−800 nm, averaging at least 10 decays at each wavelength. A 2 mL solution containing the substrate (1.0×10^{-2} M) and the sensitizer ($MeOP^+PF_6^-$, 5.0×10^{-3} M) was flashed in a quartz photolysis cell while nitrogen was bubbling through them. The experimental error was ±10%.

Cyclic Voltammetry. E_p values were obtained by cyclic voltammetry experiments, conducted with an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (cyclic voltammetry at 100 mV s^{-1}, 1 mm diameter platinum disk anode and SCE as reference) in CH_3CN−$LiClO_4$ (0.1 M).

Computational Methodology. Quantum mechanical calculations were carried out by using the Gaussian 09 package.[18] Charge and spin density distribution of the radical cations were obtained by using the B3LYP functional, after geometrical optimization performed with the same DFT model. All calculations were performed with a 6-311G(d,p) basis set.[39]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01052.

Time-resolved absorption spectra after LFP of the $MeOP^+$/**1a**, **1c** systems with and without TBAN, $MeOP^+$/**1b** system in O_2-equilibrated CH_3CN and dicumyl peroxide peroxide in the presence of **1b**; decay kinetics of **1a**$^{+\bullet}$ in the presence of TBAN in N_2- and O_2-equilibrated CH_3CN; most stable conformers for **1a**$^{+\bullet}$ and **1c**$^{+\bullet}$; SOMO of the energy minimum conformers of

$1a^{+•}$ and **$1c^{+•}$**; ^{1}H NMR and ^{13}C NMR spectra of 4-CN-$C_6H_4CH_2SCH_3$ (**1c**) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tiziana.delgiacco@unipg.it.

Notes

The authors declare no competing financial interest.

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